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(71) Applicants (*for all designated States except US*): **AB VOLVO** [SE/SE]; S-405 08 Göteborg (SE). **ENKLAVEN AB** [SE/SE]; Box 5006, S-402 21 Göteborg (SE).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **JOBSON Edward** [SE/SE]; Jägarvägen 5, S-442 77 Romelanda (SE). **HEED, Björn** [SE/SE]; Utlandagatan 19, S-412 61 Göteborg (SE).

(74) Agents: **ANDERSSON, Per** et al.; Albihns Göteborg AB, P.O. Box 142, S-401 22 Göteborg (SE).

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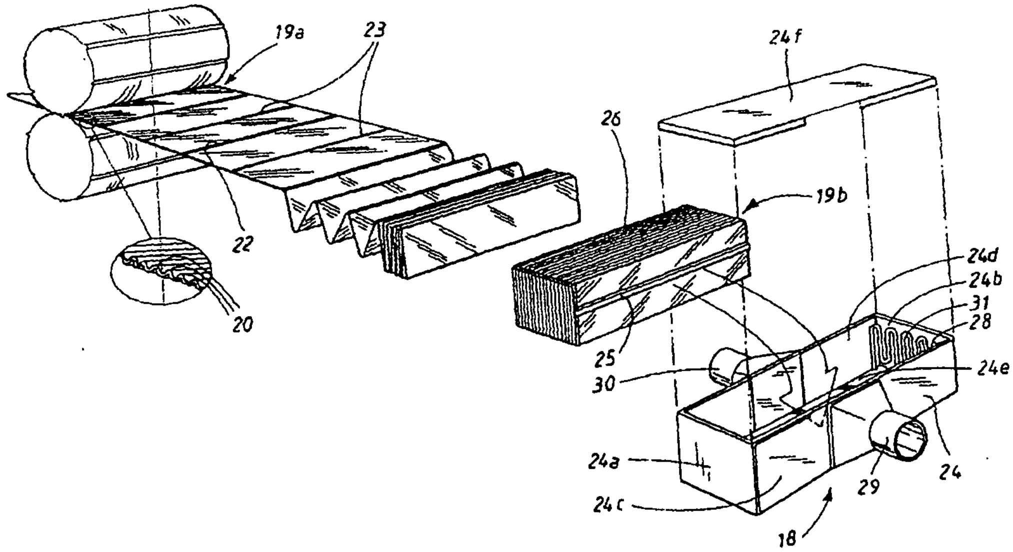
(54) Title: PROCEDURE AND DEVICE FOR TREATMENT OF A GAS FLOW



(57) Abstract: The invention relates to a method for treatment of a gas flow, comprising: guiding the gas flow through a gas treatment unit (18) adapted for filtering particles in said gas flow, and eliminating said particles in said gas treatment unit (18). The invention is characterized in that it comprises filtering particles in said gas flow by means of accumulating said particles in, or in connection with, a number of ducts (21) forming part of the gas treatment unit (21) during passage of the gas flow through the gas treatment unit (18), controlling the temperature of said gas flow along said ducts (21) to a value which provides combustion of said particles, and eliminating said filtered particles in said gas treatment unit (18) by means of combustion in said ducts (21). The invention also relates to device for accomplishing said method. By means of the invention, an improved treatment of a gas flow is provided, in particular in connection with exhaust gas purification in a diesel engine, for eliminating particles in its exhaust gases.

WO 02/29218 A1

15. The air purification system as recited in claim 1 wherein the air purification system is at room temperature.

Procedure and device for treatment of a gas flow

TECHNICAL FIELD:

The present invention relates to a method for treatment of a gas flow, comprising guiding the gas flow through a gas treatment unit adapted for filtering particles in said gas flow, and eliminating said particles in said gas treatment unit. The invention is particularly intended to be used for separating and eliminating particles in the exhaust gases from a combustion engine. The invention also relates to a device for accomplishing such a treatment of a gas flow.

BACKGROUND OF THE INVENTION:

In the field of vehicles which are operated by combustion engines, there is a general demand for low emissions of harmful substances in the exhaust gases from the engine. Said substances are primarily constituted by pollutants in the form of oxides of nitrogen (NO_x), hydrocarbon compounds (HC), and carbon monoxide (CO). As regards petrol engines, the exhaust gases are normally purified by means of an exhaust catalyst which forms part of the exhaust system and through which the exhaust gases are guided. In a so-called three-way catalyst, which is previously known, the major part of the above-mentioned harmful compounds is eliminated by means of known catalytic reactions. In order to optimise the function of the catalyst so that it provides an optimal degree of purification for NO_x, HC, and CO, the engine is in most operating conditions operated by a stoichiometric air/fuel mixture, i.e. a mixture where $\lambda=1$.

Furthermore, in the field of vehicles which are operated by means of a combustion engine, there is a demand for

16. An air purification system comprising:

a container having an inlet and an outlet;

a porous substrate inside said container;

a device for drawing a fluid into said container through said inlet, flowing said fluid through said porous substrate, and expelling said fluid out of said container through said outlet;

a manganese oxide/titanium dioxide catalytic coating applied on said substrate, said manganese oxide/titanium dioxide coating including manganese oxide on titanium dioxide, and said manganese oxide lowers an energy barrier for decomposition of ozone to oxygen; and

an ultraviolet light source to activate said catalytic coating, and photons from said ultraviolet light source are absorbed by said manganese oxide/titanium dioxide catalytic coating to form a reactive hydroxyl radical, and said reactive hydroxyl radical oxidizes contaminants in said fluid that are adsorbed onto said manganese oxide/titanium dioxide catalytic coating when activated by said light ultraviolet light source to water and carbon dioxide in the presence of water and oxygen.

low emissions of harmful emissions in the form of solid particles, primarily in the form of carbon particles, in the engine exhaust gases. This demand is for example valid in connection with diesel engines. In order to eliminate such particles, it is previously known to utilize various types of carbon filters. For example, ceramic filters are utilized today which are constructed with a porous wall structure by means of which particles in the exhaust gases can be deposited in the pores of the wall structure.

One disadvantage as regards a ceramic filter is that it must be regenerated at regular intervals, i.e. the particles which have been accumulated in the filter must be removed from the wall structure after some time of use. In this case, the regeneration suitably takes place by means of combustion of the particles at a certain increased temperature, normally 400-500° C, which for example can be obtained by means of a special electric heater. After this measure, the filter can once again be utilized for accumulating particles.

One particular type of particle filter is the so-called "city filter", by means of which the necessary temperature can be obtained so that said combustion of particles can take place. Although this type of filter in principle functions satisfactorily, it has certain disadvantages, e.g. that it on account of its construction discloses a comparatively high fall of pressure. Furthermore, it has a comparatively low filtration capacity by means of the fact that it is based on surface filtration along a comparatively small surface. Furthermore, the pressure loss over such a filter increases over the years, which is due to the fact that ashes gradually obstruct the filter. In addition, carbon can be accumulated during operation at low temperatures. When the vehicle subsequently increases the

17. A method of purifying air comprising the steps of:

applying a manganese oxide/titanium dioxide catalytic coating applied on a substrate, said manganese oxide/titanium dioxide coating including manganese oxide on titanium dioxide;

activating said manganese oxide/titanium dioxide catalytic coating;

forming a reactive hydroxyl radical;

adsorbing contaminants onto said manganese oxide/titanium dioxide catalytic coating;

oxidizing said contaminants with said hydroxyl radical;

lowering an energy barrier of decomposition of ozone with said manganese oxide of said manganese oxide/titanium dioxide catalytic coating; and

then decomposing said ozone to oxygen.

load, spontaneous ignition may occur, wherein there is a risk of the filter being damaged permanently.

There are also other types of filters which are based on the fact that particles are gradually accumulated in a filter unit, which in that case is replaced after some time of use.

SUMMARY OF THE INVENTION:

The object of the present invention is to provide an improved treatment of a gas flow, in particular during exhaust gas purification in the form of particle filtration in connection with a combustion engine, by means of which the above-mentioned problems are solved in an effective manner. This is accomplished by means of a method as initially mentioned, the characterizing features of which will be apparent from appended claim 1. The object is also accomplished by means of a device as initially mentioned, the characterizing features of which will be apparent from appended claim 12.

The method according to the invention comprises guiding the gas flow through a gas treatment unit adapted for filtering particles in said gas flow, and eliminating said particles in said gas treatment unit. The invention is characterized in that it comprises filtering particles in said gas flow by accumulating said particles in, or in connection with, a number of ducts forming part of the gas treatment unit during passage of the gas flow through the gas treatment unit, controlling the temperature of said gas flow along said ducts to a value which provides combustion of said particles, and eliminating said filtered particles in said gas treatment unit by means of combustion in said ducts. The invention also relates to device for accomplishing such a treatment of a gas flow.

ABSTRACT OF THE DISCLOSURE

A manganese oxide/titanium dioxide photocatalytic/thermocatalytic coating simultaneously oxidizes volatile organic compounds and decomposes ozone that adsorb onto the coating into water, carbon dioxide, and other substances. The manganese oxide is nano-sized. When photons of the ultraviolet light are absorbed by the manganese oxide/titanium dioxide coating, reactive hydroxyl radicals are formed. When a contaminant is adsorbed onto the manganese oxide/titanium dioxide coating, the hydroxyl radical oxidizes the contaminant to produce water, carbon dioxide, and other substances. Manganese oxide lowers the energy barrier required for ozone decomposition, decomposing the ozone to molecular oxygen. Therefore, the manganese oxide/titanium dioxide coating can also simultaneously decompose ozone to oxygen.

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The invention is based on the fact that particles are accumulated in corrugations in said gas treatment unit and are kept in place while combustion of the particles takes place. Furthermore, the invention is provided with a heat exchanging function by means of which it is controlled that a combustion of the particles takes place at a sufficiently high temperature, which in turn is provided in an energy-saving manner. During the combustion, almost exclusively carbon dioxide is formed. Thus, according to the invention, a combined method for interchange of heat and filtration of particles is provided.

In this connection, the term "particles" is used in order to describe undesired emissions of solid particles in the form of primarily carbon which normally form part of the exhaust gases from a diesel engine or a corresponding engine which is adapted for operation with a surplus of oxygen.

Advantageous embodiments of the invention will be apparent from the appended dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS:

The invention will be further described in the following with reference to a preferred embodiment and to the annexed drawings, in which

Fig. 1 shows a simplified and principal view of an engine arrangement in which the present invention can be utilized,

Fig. 2 shows a manner of constructing a special exhaust gas treatment unit which is utilized according to the invention,

Title: Bifunctional Manganese Oxide/Titanium Dioxide Photocatalyst/Thermocatalyst for Improving Indoor Air Quality
First Named Inventor: Wei
Application Serial No. To Be Assigned - Attorney Docket No. 60,246-219

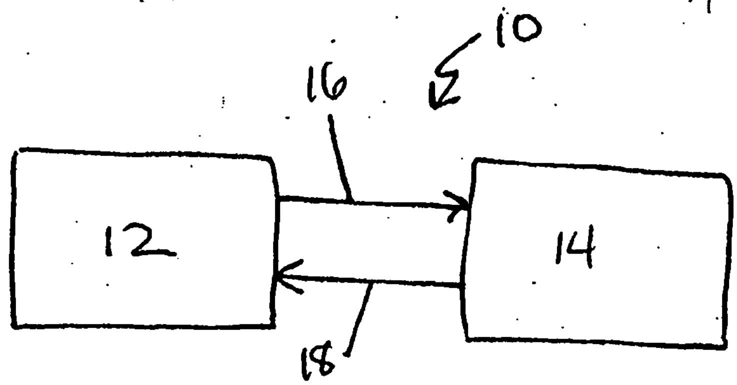

FIG. 1

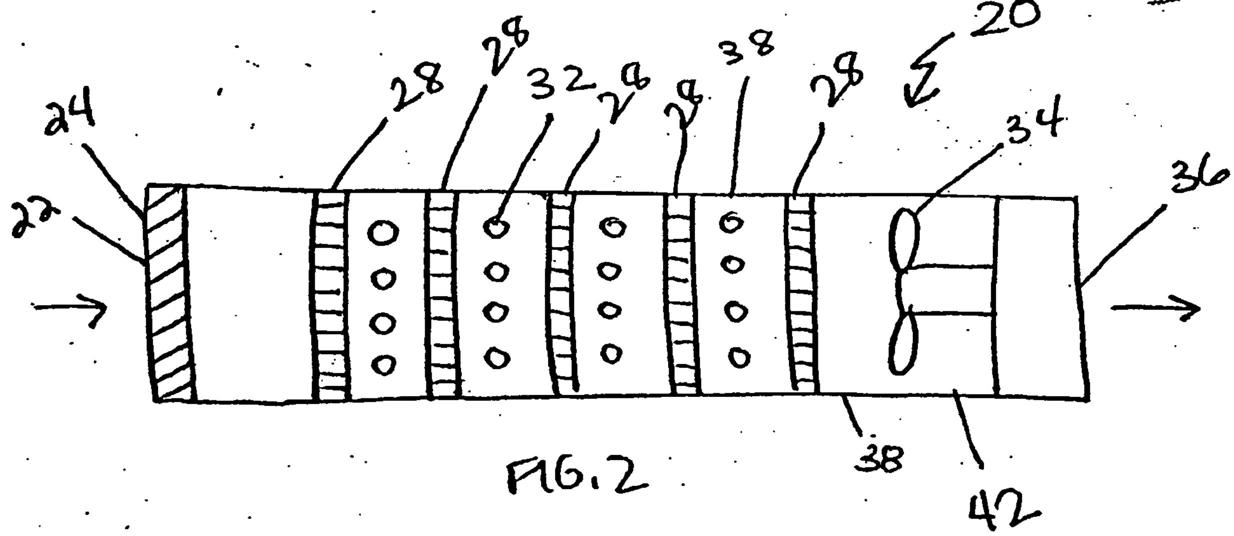

FIG. 2

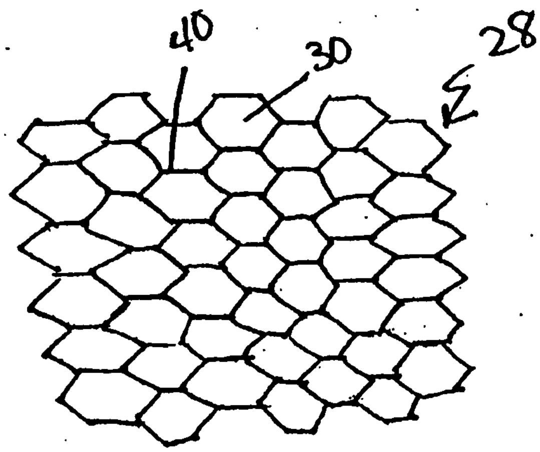

FIG. 3

Fig. 3 shows said exhaust gas treatment unit slightly enlarged in comparison with Fig. 2, and

Fig. 4 shows a detail view of said exhaust gas treatment unit.

PREFERRED EMBODIMENTS:

Fig. 1 shows a schematic and simplified view of an arrangement according to the present invention. According to a preferred embodiment, the invention is arranged in connection with a combustion engine 1 in the form of a diesel engine. However, the invention is not limited for utilization in connection with merely diesel engines, but may be utilized for all types of combustion processes where an elimination of carbon particles in a gas flow is desirable, e.g. in connection with other types of combustion engines which at least periodically are operated by a surplus of oxygen. One example of an engine type where the invention can be utilized is a so-called DI engine, i.e. an engine of the direct-injected Otto cycle engine type, which is characterized in that it in certain operating conditions is operated by a large surplus of oxygen in the air/fuel mixture to the engine. During operation of a combustion engine of, for example, the diesel engine type or the DI engine type, exhaust gases are generated which contain carbon and other solid particles, wherein there is a demand for purification of the exhaust gases in order to eliminate the particles.

The diesel engine 1 according to Fig. 1 is in a conventional manner supplied with inflowing air via an air inlet 2. Furthermore, the engine 1 is provided with a number of cylinders 3 and a corresponding number of fuel injectors 4. The respective injector 4 is connected to a central control unit 5 via a corresponding electrical connection 6. The control unit 5 is preferably computer based and is adapted to control the fuel supply to each

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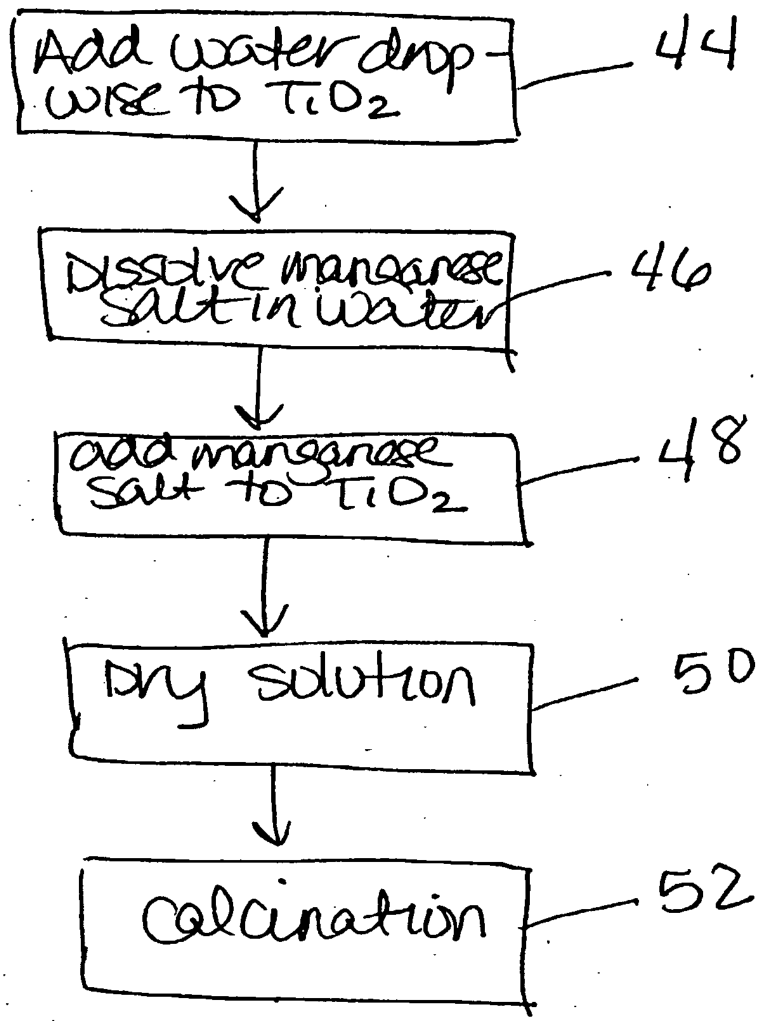


FIG. 4

injector 4 with fuel from a fuel tank 7 in a known manner so that an air/fuel mixture which is adjusted in every given moment is supplied to the engine 1, i.e. via the respective injector 4. In this regard, the control of the air/fuel mixture to the engine 1 is adjusted to the prevailing operating condition.

The control of the engine 1 takes place in an essentially known manner depending on various parameters which reflect the operating condition of the engine 1 and the vehicle in question. For example, the control of the engine can take place depending on the prevailing degree of throttle application, the engine speed, the amount of supplied air to the engine and the temperature of, for example, the cooling medium and the fuel of the engine. To this end, the control unit 5 is provided with a number of measuring signals 8. Said measuring signals 8 correspond to incoming parameters from a corresponding number of detectors, which symbolically are indicated by the reference numeral 9 in Fig. 1.

The method for controlling a diesel engine, e.g. as regards its fuel supply depending on the prevailing load and engine speed, takes place in a manner which is per se previously known and is therefore not described in further detail here. However, it can be mentioned that fuel is supplied from said fuel tank 7 and through a fuel filter 10 via a first fuel line 11. After filtering the fuel, it is guided further on to a fuel pump 12 via a second fuel line 13. From the fuel pump 12, the fuel is supplied to each injector 3 via corresponding additional fuel lines 14. The system also comprises a return line 15 for unused fuel from the respective injector 3 and back to the fuel tank 4. According to prior art, the fuel pump 12 is utilized for generating the necessary fuel pressure that is required during injection and combustion in the respective cylinder 3.

PROCESS AND APPARATUS FOR TREATING GAS CONTAINING FLUORINE-CONTAINING COMPOUNDS AND CO

BACKGROUND OF THE INVENTION

The present invention relates to a process for treating a gas containing fluorine-containing compounds and CO, and particularly it relates to a process and an apparatus for efficiently treating an exhaust gas containing fluorine-containing compounds and CO which are discharged in the step of dry cleaning the inner surfaces and the like of a semiconductor manufacturing apparatus, the step of etching various types of formed films such as oxide films and the like in the semiconductor industry.

In the semiconductor industry, various types of harmful gases are being used in the semiconductor manufacturing steps and the environmental pollution by discharging them to the environment is a matter of concern. Particularly, in an etching step, a CVD step and the like in the semiconductor industry, fluorinated hydrocarbons such as CHF_3 and fluorine-containing compounds such as perfluoro-compounds including CF_4, C_2F_6, C_3F_8, C_4F_8, C_5F_8, SF_6 and NF_3 (hereinafter referred to as "PFC") are being used. It is of urgent necessity to establish a system of removing the fluorine-containing compounds present in the exhaust gas from these steps as the global warming gases. Further, the exhaust gas from these steps sometimes contains CO as the processing gas or frequently contains CO which has been generated by exposing a mixed gas of PFC with O_2 to a plasma in a chamber.

As the method of removing PFC in a gas, a gas treating method using an alumina based catalyst obtained by incorporating various metals into alumina; a gas treating method using alumina having an Na content as the metal of not greater than 0.1% by weight; a gas treating method comprising contacting a molecular oxygen with a gas in the presence of alumina; a gas treating method using an aluminum-containing catalyst in the presence of steam at a temperature of 200 to 800°C; a gas treating method using various types of metal catalyst in the presence of a

During operation of the engine 1, its exhaust gases are guided out from the cylinders 3 via a branch pipe 16 and further on to an exhaust pipe 17 which is connected to the branch pipe 16. In accordance with the invention, a unit 18 is provided further downstream along the exhaust pipe 17 for treatment of exhaust gases, in this case in the form of exhaust gases from the engine 1. The construction and the function of this exhaust gas treatment unit 18 will be described below in detail with reference to Figs. 2, 3 and 4. From the exhaust gas treatment unit 18, the exhaust gases are guided further out into the surrounding atmosphere, according to what is indicated schematically by means of an arrow in Fig. 1.

According to what in particular is apparent from Fig. 2, the exhaust gas treatment unit 18 comprises a strip 19a of metal, which by means of a suitable method (e.g. pressing or rolling) has been formed with corrugations 20 which extend in a predetermined angle in relation to the longitudinal direction of the strip 19a. This angle can amount to 0-90°, and suitably within the interval of 30°-60°. The strip 19a is repeatedly folded in a zigzag form so that it forms a strip package 19b. In this manner, an arrangement is formed where the above-mentioned corrugations 20 run crosswise in relation to each other in adjacent layers in the strip package 19b. Moreover, the corrugations 20 function as spacers, by means of which several ducts or slits 21 (see in particular Fig. 4) are formed which are separated from each other and through which a gas flow is intended to flow, in the present case thus a flow of exhaust gases from the engine 1.

The flow pattern in the ducts 21 is of such a kind that the flow in the duct is constantly mixed and has a satisfactorily contact with the walls of the ducts 21. Moreover, according to what is shown in Fig. 2, the

molecular oxygen and water; and the like have been proposed. Furthermore, as described in the specification of Japanese Patent Application No. 2000-110668, a gas treating method using γ-alumina having a specific crystal structure (which exhibits diffraction lines having an intensity of 100 or more at the five angles of $33° \pm 1°$, $37° \pm 1°$, $40° \pm 1°$, $46° \pm 1°$ and $67° \pm 1°$ of the angles of diffraction 2θ measured by an X-ray diffraction apparatus) as the catalyst has been proposed.

On the other hand, as the method for removing CO in a gas, there is a method comprising oxidizing CO using a hopcalite oxidation catalyst (a composite oxide of Cu and Mn, an Ni oxide, and the like) and O_2 to CO_2 which is then removed. However, the technique of simultaneously treating fluorine-containing compounds and CO has not yet been reported.

Accordingly, in order to treat both fluorine-containing compounds and CO in a gas according to the conventional technique, it is necessary to adopt a method comprising forming a two-stage catalytic reaction vessel having a CO oxidation catalyst arranged in the previous stage and γ-alumina arranged in the later stage and passing a gas therethrough to oxidize CO in the previous stage and to decompose the fluorine-containing compounds in the latter stage. However, in this instance, there is a problem that the fluorine in the fluorine-containing compounds present in the gas comes to a catalytic poison against the CO oxidation catalyst to remarkably lower the CO oxidative power in the reaction vessel of the previous stage and as a result, the CO cannot be treated to a threshold limit value-time weighted average concentration (TLV-TWA value) of 25 ppm or smaller in a short period of time.

Furthermore, in order to treat a gas containing fluorine- containing compounds and CO according to the conventional technique, there are such problems that each component has to be treated with a different catalyst, which needs to use different heating vessels to be

corrugations 20 can, in order to facilitate the folding of the strip, be interrupted at regular intervals in order to be replaced with folding notches 22, 23 which run at right angles to the strip 19a.

Furthermore, the strip 19a is enclosed in a heat insulated external container 24 (the insulation is not shown in the drawings). Said external container 24 is essentially rectangular and comprises two end walls 24a, 24b, two sidewalls 24c, 24d, a lower wall 24e, and an upper wall 24f. The strip package is sealed against the two sides 25, 26 which are arranged in parallel with the flow direction of the gas flow through the strip package. However, the end sections of the strip package are not sealed, but end in two return chambers 27, 28, according to what is apparent from in particular Fig. 3.

Furthermore, the external container 24 comprises an inlet which is provided with a sleeve 29 for connection of inflowing gas and an outlet which is provided with an additional sleeve 30 for connection of outflowing gas. By means of the folding of the strip, connection takes place in a simple manner from the side of the package to all ducts on one side of the strip package 19b, which is due to the fact that the two nozzles 19, 30 connect to a respective side of the strip. The inlet and outlet, respectively, of the external container 24 are preferably situated essentially centrally on the respective sidewall 24c, 24d. This corresponds to the fact that the inlet and the outlet, respectively, are positioned at essentially the same distance from the respective end wall, 24a, 24b. By means of this division of the gas flow in two flows with only half the speed, the pressure loss decreases considerably.

According to the present invention, the strip package 19b is utilized for filtering and eliminating particles,

individually filled with different catalysts, and the treating temperature for each heating vessel has to be individually controlled, and further a wide space for installing the apparatuses is necessary, and the temperature control becomes complicated. Further, there is a problem of complicating the control of catalysts since the period of exchanging the catalyst differs due to the difference in the lives of individual catalysts. In addition, there is a problem of an increase in the running cost such as the expense necessary for periodically exchanging the catalysts.

Then, the object of the present invention is to solve the above described problems according to the conventional technique and to provide a process and an apparatus for treating a gas containing fluorine-containing compounds and CO which can simultaneously and efficiently treat fluorine-containing compounds and CO and are low in the running cost and can be simply controlled.

SUMMARY OF THE INVENTION

In order to solve the above described problems, the present inventors have made strenuous investigations, and found that the above described object can be achieved by first reacting a gas containing fluorine-containing compounds and CO with O_2 and H_2O without using a CO treating catalyst at a specified temperature or higher to oxidize the CO to CO_2, and then contacting the gas with γ-alumina as the catalyst to decompose the fluorine-containing compounds, in treating the gas containing the fluorine-containing compounds and CO.

Namely, according to the present invention, there is provided a process for treating a gas containing fluorine-containing compounds and CO which comprises contacting the above described gas with O_2 and H_2O at a temperature of 850°C or higher to oxidize the CO to CO_2; and subsequently contacting the gas with γ-alumina heated at 600 to 900°C to decompose the fluorine-containing compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic perspective view showing one

primarily in the form of carbon, from the exhaust gases which are emitted from the engine 1 and guided into the exhaust gas treatment unit 18 via the exhaust pipe 17 (cf. Fig. 1). More precisely, the strip package 19b is formed in such manner that particles in this exhaust gas flow will be accumulated in the above-mentioned corrugations 20, which in this way function as separation elements by means of which said particles can be separated from the gas flow. The invention is based on the fact that the corrugations are utilized for collecting the particles, which will remain in place along the corrugations 20 for a sufficiently long time, so that they eventually will be combusted. This accumulation of particles on the strip package 19b takes place by means of the fact that the exhaust gas is repeatedly relinked to a new direction of motion by means of which the particles will show a tendency to fall out of the exhaust gas stream and instead adhere to the surface of the strip package 19b, i.e. along the corrugations 20. This accumulating function of the exhaust gas treatment unit 18 is obtained on the one hand by means of the fact that the particles, due to their comparatively high density, have a tendency to move in a more linear manner than the gas, and on the other hand by means of the fact that particles which come close to the surface or the wall will be attracted by it. The latter takes place by means of e.g. electrical forces and so-called van der Waals forces. Furthermore, the turbulent flow which the corrugations cause results in that the gas is constantly mixed so that all particles eventually will come close to the wall.

Furthermore, according to what will be described in detail below, an increased temperature (normally approximately 400-500° C) can be generated in the strip package 19b during operation of the engine 1. This can take place either by means of a special control of the

preferred embodiment of the apparatus for treating a gas containing fluorine-containing compounds and CO according to the present invention. In Fig. 1, each referential numerals have the following meaning.

1: PFC exhaust gas treating apparatus;
20: heat oxidation vessel;
20b: oxidation reaction zone;
21: PFC exhaust gas inlet;
22: O_2 inlet;
23: H_2O inlet;
28: ceramic heater;
29: baffles;
30: catalytic reaction vessel;
31: γ-alumina;
32: ceramic heater;

DETAILED DESCRIPTION OF THE INVENTION

The gas containing fluorine-containing compounds and CO which can be treated by the present invention may include exhaust gases which are discharged in the step of dry cleaning the inner surfaces of a semiconductor manufacturing apparatus and the step of etching various types of formed films in the semiconductor industry and the like. Further, the above described fluorine-containing compounds may include fluorinated hydrocarbons such as such CHF_3, perfluoro-compounds such as CF_4, C_2F_6, C_3F_8, C_4F_8, C_5F_8, SF_6 and NF_3 and the like.

In the present invention, the temperature at which the above described gas is contacted with O_2 and H_2O is 850°C or higher, preferably 870°C or higher. When the temperature is lower than 850°C, the CO in the gas is not sufficiently oxidized and remains, and thus such temperatures are not preferred.

In the present invention, the gas containing fluorine-containing compounds and CO (hereinafter referred to as "PFC exhaust gas" for brevity) is first contacted with O_2 and H_2O at the above described temperature to cause the reactions in the gas phase as shown by the following formulae, whereby CO is oxidized to CO_2.

composition of the exhaust gases (which in turn can take place by injecting for example hydrocarbon compounds in the exhaust flow, or by means of a special control of the engine 1) or by means of a special heater element or by means of a heat exchanging function of the strip package 19b (or by means of a combination of these measures). All in all, this results in that particles which have been accumulated in the corrugations 20 will be combusted either continuously or intermittently when the temperature is sufficiently high. During the combustion, the particles are in this way eliminated while carbon dioxide is formed.

It can be noted that a surplus of oxygen is necessary in the exhaust gas while the accumulated particles are combusted. Thus, the invention can be utilized for engines which are adapted for operation with a surplus of oxygen (i.e. $\lambda>1$), but also for engines adapted for operation with an equilibrium of oxygen ($\lambda=1$) or a deficit of oxygen ($\lambda=1$). In the latter cases, combustion of carbon and other particles suitably can take place during intermittent occasions with a surplus of oxygen.

The invention can be utilized with various methods for filtration and separation of carbon particles from the gas flow in question. Below, some examples of methods for carbon separation will be described. According to a first embodiment, the invention can be utilized for providing a filtering process of the surface filtering type in which particles are accumulated in a coat or a layer, in this case on the ~~surface of the strip package 19b.~~ In order to provide this, preferably a porous catalytic coating or wall, suitably in the form of a (not shown) glass fibre mat or similar, can be laid out between the folds in the strip package 19b. Said mat can be provided along the entire extension of the strip package 19b, or at certain selected parts of the strip package 19b. Preferably, said

$2CO + O_2 \rightarrow 2CO_2$

$CO + H_2O \rightarrow CO_2 + H_2$

$2H_2 + O_2 \rightarrow 2H_2O$

Subsequently, the gas is then contacted with γ-alumina at a temperature of 600 to 900°C, by which, the fluorine- containing compounds in the gas is decomposed. For example, when the gas contains CF_4 as the PFC, the CF_4 is decomposed to CO_2 and HF by the reaction as shown by the following formula.

$CF_4 + 2H_2O \rightarrow CO_2 + 4HF$

In the present invention, the amounts of O_2 and H_2O to be contacted with a PFC exhaust gas are preferably sufficient to decompose all of CO and fluorine-containing compounds in the PFC exhaust gas to be treated to CO_2 and HF. In a preferred embodiment, the amount of O_2 to be added to the PFC exhaust gas is preferably at least molar amount necessary for the C atoms in the fluorine-containing compounds and the C atoms of CO which are present in the PFC exhaust gas to come to CO_2 (minimum molar amount), more preferably the amount of at least molar amount obtained by adding one mole to the minimum molar amount. Further, the amount of H_2O to be added to the PFC exhaust gas is preferably at least molar amount necessary for the F atoms in the fluorine-containing compounds to come to HF (minimum molar amount), more preferably, the molar amount corresponding to 6 to 20 times of one mole of the fluorine-containing compounds. In this instance, H_2O is preferably introduced in a gaseous state and, for example, H_2O is sent from an H_2O tank to a vaporizer by means of a pump and heated to 100°C or higher to render the entire amount steam, and furthermore it is preferred to introduce an H_2O with a pressure of an inert gas such as N_2.

In the present invention, the γ-alumina to be contacted with the PFC exhaust gas acts as a catalyst for decomposing fluorine-containing compounds. In the present invention, the contact of the PFC exhaust gas with γ-alumina is preferably conducted at a temperature of 600 to

mat is provided between the surfaces of the strip package 19b (cf. Fig. 4), i.e. without this being in contact with the surfaces of the strip package 19b, by means of which the gas flow is influenced to pass through the mat. If the mat for example is laid out close to the respective return chamber 27, 28, it will be possible to control the temperature by means of a suitable engine control, according to what will be described in detail below. In this manner, the combustion of particles can be controlled. A similar function is obtained if the strip package 19b is provided with a fibre cloth, a net or some similar ~~porous coat~~, ~~which is capable of absorbing particles.~~

The basic principle of utilizing the above-mentioned mat is that the particles which are present in the gas flow will be accumulated and kept in the mat so that they can be combusted. According to a variant of this embodiment, said mat can be formed of catalytic material, which improves the filtering effect.

An alternative manner of separating particles is by providing the exhaust gas treatment unit 18 with a porous body which can be of a suitable material, e.g. foam, ceramic or a sand bed and which can be situated at a suitable place within its container 24. Such a type of filtering is of the deep filtering type, in contrast to filtering methods where particles are accumulated in a coat or a layer, which in that case is termed surface filtering according to what has been explained above.

One additional manner of separating particles in the exhaust gas treatment unit 18 according to the invention is to use the principle of electric filter, which is particularly suitable for filtration of comparatively small particles, more precisely of the order of <1µm. An electric filter is based on the utilization of a special

900°C, preferably 650 to 850°C, more preferably 750°C. When the contact temperature of the PFC exhaust gas with the γ-alumina is lower than 600°C, the activity of the alumina as a catalyst is lowered to decrease the decomposition ratio of the PFC, and thus such temperatures are not suitable, and conversely temperatures of higher than 900°C cause crystal transition and there is a fear of vitrifying the γ-alumina, and thus such temperatures are not suitable. It is preferred to heat the γ-alumina catalyst to the above described temperature by a heating means.

As the γ-alumina which can be used in the present invention, the γ-alumina having a crystal structure which exhibits diffraction lines having an intensity of 100 or more at five angles of 33° ± 1°, 37° ± 1°, 40° ± 1°, 46° ± 1° and 67° ± 1° of the angles of diffraction 2θ measured by an X-ray diffraction apparatus as proposed in Japanese Patent Application No. 2000-110668 can be preferably used. The Na_2O content in the alumina is preferably not greater than 0.02% by weight based on the entire amount of the γ-alumina in consideration of the decomposition performance of the fluorine-containing compounds. The γ-alumina having such a crystal structure can be obtained, for example, by firing an alumina sol as the spherical alumina hydrogel $[Al(OH)_y \cdot nH_2O]$. Although the γ-alumina which is used in the present invention is not particularly limited in its shape as far as it has the above described crystal structure, it is preferably spherical from the standpoint of handling properties. Further, although the particle size of the γ-alumina may be within the range which does not increase a pressure drop when the gas to be treated is passed, it is preferably fine to increase the contact area with the gas components to be treated and is preferably in the range of 0.8 mm to 2.6 mm.

Further, according to the present invention, there is provided an apparatus for treating a gas containing fluorine- containing compounds and CO. The apparatus for treating a gas containing fluorine-containing compounds

ionization unit (not shown in the drawings) which in that case suitably is provided in connection with the exhaust gas treatment unit 18, for example before (i.e. upstream of) the strip package 19b. Said ionization unit is per se previously known and is utilized for charging particles in the passing gas by means of ionization of the gas. Then, the charged particles can be influenced to fall out and be accumulated on earthed plates. In that case, according to a suitable form of the invention, said earthed plates are constituted by the actual strip package 19b, which to this end is connected to a (not shown) ground point. However, this variant of the invention is not limited to the ionization unit being situated upstream of the strip package 19b. Alternative placings, e.g. in one of the above-mentioned return chambers 27, 28, can also be suitable placings for such an ionization unit. The advantage as regards ionization of the gas in one of the return chambers 27, 28 (or both) is that the main part of the carbon particles in this way falls out close to the respective return chamber where the temperature is favourable for combustion of the particles. By placing the ionization unit before the strip package 19b, only one single small ionization unit is required, while two such units are required if ionization shall take place in the two return chambers 27, 28.

In order to facilitate filtering, an aggregation of small particles to larger particles can take place. This takes place by utilizing turbulence in the exhaust gas treatment unit 18. This takes place by means of the turbulence of the gas flow which the corrugations in the separation unit cause. Particles collide with each other and with the walls, by means of which electricity is transmitted. In this manner, attractive electric fields are formed. These large particles are subsequently

and CO comprises a heat oxidation vessel having a hollow inside enabling the passage of the above described gas therethrough, a heating means capable of heating the temperature of the gas in the above described hollow inside to 850°C or higher, a gas inlet, an O_2 inlet and an H_2O inlet; and a catalytic reaction vessel which is under fluid-communicating condition with the above-described heat oxidation vessel and has been filled with γ-alumina.

In the PFC exhaust gas treating apparatus of the present invention, the heat oxidation vessel and the catalytic reaction vessel may be arranged under fluid-communicating condition, and they may be formed as one body or as separate bodies. Further, although the material of the heat oxidation vessel and the catalytic reaction vessel is not particularly limited, it is preferably formed of a material which is stable in a high temperature atmosphere and inert to the gas components to be treated and, simultaneously, excels in thermal conductivity, and particularly preferably formed of stainless steel.

In the PFC exhaust gas treating apparatus of the present invention, a heating means of the heat oxidation vessel is not particularly limited as far as it can heat the gas phase portion formed in the hollow inside of the heat oxidation vessel to 850°C or higher, preferably to 870°C or higher and, for example, a ceramic heater such as a ceramic electric tubular furnace is preferably arranged on the outside of the heat oxidation vessel.

In the heat oxidation vessel of the PFC exhaust gas treating apparatus of the present invention, at least a PFC exhaust gas inlet, an O_2 inlet and an H_2O inlet are provided. These inlets are preferably provided at the top portion of the heat oxidation vessel, and each is connected to a PFC exhaust gas generation source such as an exhaust gas line from a semiconductor manufacturing apparatus, an O_2 supply source, or an H_2O supply source through piping. It is preferred to introduce H_2O in a gaseous form, and thus in a preferred embodiment, the H_2O

filtered out by means of one of the above-mentioned methods.

As mentioned above, a basic principle of the invention is that the particles which have been separated by means of the strip package 19b also can be eliminated in the exhaust gas treatment unit 18. Preferably, this takes place by means of combustion in the strip package 19b. In that case, the basic principle is that the invention is utilized in connection with such a control of the engine 1 that a temperature, which is sufficiently high for combustion of the particles, is generated in the exhaust gases, and thus also in the strip package 19b. On account of this, there is a demand for accurate temperature control of the exhaust gases. To this end, a basic principle of the invention is that an adjustment of the temperature of the prevailing gas flow takes place so that the temperature of active parts of the exhaust gas treatment unit 18 will be above a predetermined temperature limit at which combustion of particles can take place. As regards the heat exchanging function, it can be established that various parts of the exhaust gas treatment unit 18 normally have varying temperatures. More precisely, the temperature in the respective return chamber and its vicinity is normally higher than in the parts of the exhaust gas treatment unit 18 where the gas is guided in and out. The temperature limit at which combustion takes place is normally approximately 400-500° C. In order to achieve an increase of the temperature of the exhaust gas treatment unit 18, exothermic reactions, which occur as a consequence of the energy content in the exhaust gases, are utilized. Furthermore, an increase of the temperature can be obtained as a result of a change of the energy content in the exhaust gases by means of a suitable engine control, wherein the control unit 5 is utilized for this control. More precisely, this can be achieved by means of, for

supply line to be connected to the H_2O inlet is constituted of an H_2O (liquid) tank of the H_2O supply source, a vaporizer which vaporizes the liquid H_2O to be supplied from the H_2O tank, a piping which connects the tank with the vaporizer, a water pump provided on the piping, and a supply source of an inert gas such as N_2 for pumping the vaporized H_2O to the H_2O inlet of the heat oxidation vessel, and a heating means such as a band heater is installed on the piping connected to the H_2O inlet.

Further, it is preferred to install a contact auxiliary means to enhance the contact efficiency of the CO in the gas with O_2 and H_2O in the inside of the heat oxidation vessel. The contact auxiliary means is not particularly limited as far as it can cause a turbulence in the gas phase portion to be formed in the hollow inside of the heat oxidation vessel and may include, for example, baffles formed by arranging a plurality of plates, fins or the like on the inner wall of the heat oxidation vessel spirally or alternately so as to face one another in the radial direction, fillers having a small pressure loss and the like. In the case of using baffles as the contact auxiliary means, the surfaces of the baffles may be coated with a metal such as Ni.

The catalytic reaction vessel of the PFC exhaust gas treating apparatus of the present invention is filled with γ-alumina. The volume of the catalytic reaction vessel is not particularly limited as far as it can be filled with γ-alumina. As the γ-alumina to be filled in the catalytic reaction vessel, the γ-alumina having the above described specified crystal structure can preferably be used.

Further, in a preferred embodiment, the catalytic reaction vessel is provided with a heating means to heat γ-alumina to 600 to 900°C, preferably 650 to 850°C, more preferably 750°C. This heating means is not particularly limited and the same heating means as provided in the heat oxidation vessel can be used, and the heating means as described above in connection with the heat oxidation

example, a modification of the time for the injection and the ignition in the respective cylinder, or by means of additional injection of fuel during the exhaust stroke of the engine. An additional manner of providing an increase of temperature is by injecting air from an external source (not shown) into the exhaust gas treatment unit 18 during rich operation of the engine. An additional manner of providing an increase of temperature is by controlling the cylinders individually, wherein the exhaust gases from one or some of the cylinders 3 are operated in a rich manner whereas the rest of the cylinders are operated in a lean manner. This can result in a powerful exothermic reaction and a heat release.

The combustion of particles is facilitated if the strip package 19b is coated with some type of oxidation catalyst, or some other suitable type of catalyst, which provides catalytic oxidation of predetermined gas components, e.g. in the form of hydrocarbon compounds in the exhaust gases. In this way, the presence of such hydrocarbon compounds can be influenced by controlling the engine so that large contents of uncombusted hydrocarbons are generated in the exhaust gas. By means of oxidation of these hydrocarbons in the exhaust gas treatment unit 18, a drastic increase in temperature in the exhaust gas treatment unit is obtained, which in turn results in an effective particle combustion.

In case of the invention being utilized in diesel engines, it is not always suitable to operate the engine in a rich manner. In such a case, an increase in temperature can instead be obtained by injecting fuel directly into the exhaust gases after the engine or in connection with the exhaust stroke in the engine. In one such case, fuel (or some other reducing agent) can be dosed both before the exhaust gas treatment unit 18, e.g. in one of the return chambers 27, 28, and directly into

vessel can be preferably be used.

Moreover, if necessary or required, the PFC exhaust gas treating apparatus of the present invention may be combined with an apparatus for separating solid substances such as a water splaying tower to separate solid substances which might be present in the gas, or an apparatus for removing an acid gas such as a water splaying tower to remove an acid gas such as HF to be obtained after the PFC exhaust gas treatment of the present invention.

With reference to the Figure attached hereto, the PFC exhaust gas treating apparatus of the present invention will now be explained in more detail but the present invention should not be limited thereto. In the following description, in order to simplify the explanation, fluorine-containing compounds are supposed to be perfluoro-compounds such as CF_4 and abbreviated to merely "PFC" for explanation.

Fig. 1 is a schematic view showing one preferred embodiment of the PFC exhaust gas treating apparatus of the present invention. The PFC exhaust gas treating apparatus of the present invention 10 has a heat oxidation vessel 20 which allows a PFC exhaust gas to contact with O_2 and H_2O at a temperature of 850°C or higher to effect oxidation treatment of CO in the gas, and a catalytic reaction vessel 30 which allows the oxidation treated gas to contact with γ-alumina at a temperature of 600 to 900°C to decompose the PFC in the gas. The heat oxidation vessel 20 and the catalytic reaction vessel 30 are arranged in such a fluid-communicating condition that the PFC exhaust gas flows down from the heat oxidation vessel 20 arranged at the upper stage to the catalytic reaction vessel 30 arranged at the lower stage. In the present embodiment, the heat oxidation vessel 20 and the catalytic reaction vessel 30 comprise cylindrical stainless steel mini-columns having the same size.

At the top portion 20a of the heat oxidation vessel 20, a gas inlet 21, an O_2 inlet 22 and an H_2O inlet 23 are

the exhaust gas treatment unit 18 between its inlet and the return chambers 27, 28 (or between the return chambers and their outlets).

Regardless of which method for heating the exhaust gases is utilized, it can be established that the invention is based on the fact that the engine 1 can be operated so that a sufficiently high temperature is generated in the strip package 19b, which in turn results in a combustion of the particles which have been accumulated in the corrugations 20. In this connection, the strip package 19b functions as a heat exchanger, wherein the exhaust gas flow takes place during interchange of heat between incoming and outgoing flows. The interchange of heat according to the invention is based on the fact that a sufficiently high temperature can be obtained with a comparatively low consumption of energy. In this way, this temperature exceeds a level at which the reaction of combustion can take place. More precisely, the interchange of heat can be utilized in order to provide a higher exhaust gas temperature than the exhaust gases have before they are guided into the exhaust gas treatment unit 18. Furthermore, the invention is based on the fact that the particles are accumulated and kept in the exhaust gas treatment unit 18 for a sufficiently long time in order for a combustion of the particles to take place at a temperature in the order of 400-500° C.

An additional possible manner of increasing the temperature of the gas flow is by means of externally supplied heat. According to what is shown in Figs. 2 and 3, this can, for example, take place by means of a special heater element 31. In that case, such a heater element 31 is suitably provided in each one of the return chambers 27, 28. The heater element 31 is formed of electrical heating conductors which are adapted for generating heat during connection to a separate (not

provided. The gas inlet 21 is connected to a PFC exhaust gas supply source (not shown in the Figure) such as an exhaust gas line of a semiconductor manufacturing apparatus through piping. The O_2 inlet 22 is connected to an O_2 supply source (not shown in the Figure) through piping. The H_2O inlet 23 is connected to a vaporizer 25 through piping 24 wrapped with a band heater, and the vaporizer 25 is connected to an H_2O (liquid) tank 26 through piping on which a water pump 27 is installed. In addition, the vaporizer 25 is connected to an inert gas (N_2) supply source through piping.

The inside of the heat oxidation vessel 20 is rendered hollow, and the hollow inside has an oxidation reaction zone 20b into which an PFC exhaust gas, O_2 and H_2O are introduced to advance the oxidation reaction of CO. The oxidation reaction zone 20b has a plurality of baffles 29 as the contact auxiliary means to enhance the contact efficiency of CO in the PFC exhaust gas with O_2 and H_2O. The baffles 29 are plates or fins having a size slightly longer than the inner radius of the heat oxidation vessel 20 and are spirally arranged on the inner wall of the heat oxidation vessel 20 or are alternately arranged on the inner wall of the heat oxidation vessel 20 so as to face one another in the radial direction. At the outer periphery of the heat oxidation vessel 20, a ceramic electric tubular furnace 28 is provided as the heating means capable of heating the temperature of the oxidation reaction zone 20b to 850°C or higher. Further, in order to measure the temperature of the oxidation reaction zone, a thermocouple (not shown in the Figure) is provided at the center of the hollow inside of the heat oxidation vessel.

Downstream of the heat oxidation vessel 20, a catalytic reaction vessel 30 is provided in a fluid-communicating condition with the heat oxidation vessel 20. The inside of the catalytic reaction vessel 30 is filled with γ-alumina. The γ-alumina having the above described specific structure is preferably used.

Furthermore, at the outer periphery of the catalytic

shown) voltage source. It can in particular be noted that even a comparatively small supply of heat in the return chambers by means of the heater element 31 results in an efficient increase in temperature. Thus, by means of a comparatively small supply of heat, an increase in temperature is obtained which is sufficient for combusting the carbon particles which have been filtered out.

The invention is not limited for utilization with the above-mentioned heater element. Alternatively, heat can be supplied externally by means of a gas or oil burner or an external fuel injection, which, however, are not shown in the drawings. According to an additional alternative, a heating function can be provided by means of a (not shown) supply of hot air (or some other suitable gas) from an external source.

Furthermore, the invention is not limited for utilization with an external supply of heat. Thus, such a supply can in principle be excluded for those applications in which a sufficiently high temperature can be generated without any externally supplied heat.

Thus, it can be established that the invention can be arranged in such manner that an increased temperature is generated by controlling the composition of the exhaust gases in a suitable manner, i.e. by selecting the concentration of various substances or gas components in the exhaust gas flow which in turn results in an increase in temperature which is necessary for elimination of particles by means of combustion. As mentioned above, this can be provided by means of an engine control which is adapted to its purpose (which in turn can be utilized for generating predetermined levels of, for example, hydrocarbon compounds in the exhaust gas flow), by means of injection of, for example, hydrocarbon compounds

reaction vessel 30, a ceramic electric tubular furnace 32 is preferably provided as the heating means capable of heating the γ-alumina at 600 to 900°C. This ceramic electric tubular furnace 32 may be either integrated with or separated from the ceramic electric tubular furnace 28 provided for the heat oxidation vessel 20. Further, in order to measure the temperature of the inside of the catalytic reaction vessel 30, a thermocouple (not shown in the Figure) is installed in the inside of the catalytic reaction vessel 30.

Examples

The present invention will be more concretely explained below on the basis of examples.

Example 1

The relationship between the temperature of the gas phase portion in a heat oxidation vessel and the removal ratio of CO was observed as the CO treatment properties in a gas with no catalyst.

As the heat oxidation vessel, a stainless steal mini-column having an inner diameter of 27 mm and a height of 500 mm amounted in a ceramic electric tubular furnace was used. In order to measure the temperature of the gas phase portion in the hollow inside of the heat oxidation vessel, a thermocouple was installed nearly at the center of the hollow inside of the heat oxidation vessel. The temperature was varied stepwise from 500 to 900°C while monitoring the temperature of the gas phase portion with the thermocouple.

Carbon monoxide (CO) diluted with N_2 which was used as an artificial test exhaust gas, O_2 and H_2O were introduced into the hollow inside of the heat oxidation vessel so as for the O_2 and H_2O to come to at least equimolar amounts at a total gas flow rate of 410 sccm. At this instance, the concentration of the CO introduced was set at 1.22 to 1.33%; that of O_2 introduced was set at 3.7 to 3.9%; and the flow velocity of H_2O was set at 0.079 mL/min. The treatment time was set at 30 minutes.

In order to observe the disposal performance in the

directly into the exhaust gases or by injecting air into the exhaust gases. Alternatively, according to what has been mentioned above, the invention can also be arranged in such manner that an increase in temperature is obtained by means of externally supplied heat.

During operation of the engine 1, exhaust gases are supplied through the exhaust gas treatment unit 18. In this case, the exhaust gases are guided via the inlet 29 (cf. Figs. 2 and 3) and are divided into two partial flows 35, 36 (cf. Fig. 3). Said flows 35, 36, are guided through the ducts on one side of the strip package 19b and in the direction of the respective return chamber 27, 28. Initially, the supplied exhaust gases will be comparatively cold, but are gradually heated towards the reaction temperature at which combustion of particles can take place, according to what has been explained above. At the same time as hot exhaust gases are guided towards the outlet 30 of the exhaust gas treatment unit 18, additional exhaust gases enter via its inlet 29. In this case, heat will be transmitted from the outgoing gas flow to the incoming gas flow. By means of a satisfactorily heat exchange between the outgoing and the incoming gas flows, the local temperatures of said flows can be influenced to lie close to each other. For this reason, only a small additional supply of heat in the return chambers 27, 28 is required in order to, for example, increase the temperature of the gas flow. At the same time as the gas flow is heat-treated to the correct temperature in the exhaust gas treatment unit 18, it is guided over the corrugations 20 which constitute a filter, wherein the particles are accumulated and finally combusted as a consequence of the increased temperature.

The invention discloses an effective heat exchanging function, which in turn is utilized for facilitating the adjustment of the temperature of the exhaust gas

heat oxidation vessel, CO, CO_2, O_2 and H_2 in the gas at the outlet of the column were analyzed using a gas chromatograph apparatus equipped with a mass detector ("AGS-7000U", manufactured by Anelva Co., Ltd.). The results are set forth in Table 1.

Table 1

Treating Tempera-ture (°C)	Gas at Inlet			Gas at Outlet				CO Removal Ratio (%)
	CO (%)	O_2 (%)	H_2O (mL/min)	CO (ppm)	CO_2 (ppm)	O_2 (%)	H_2 (ppm)	
500	1.28	3.8	0.079	11200	470	3.8	<2	13
600	1.22	3.9	0.079	9960	1470	3.8	<2	18
700	1.23	3.8	0.079	7160	3600	3.6	<2	42
750	1.27	3.8	0.079	3770	6310	3.4	<2	70
800	1.23	3.8	0.079	500	10500	3.2	<2	96
850	1.29	3.8	0.079	12	9470	3.2	<2	99.9
870	1.28	3.7	0.079	<2	11000	3.2	<2	100
900	1.31	3.9	0.079	<2	11300	2.9	<2	100

As would be understood from Table 1, when the temperature of the gas phase portion of the heat oxidation vessel was 850°C, CO was reduced to 12 ppm (removal ratio of 99.9%) which was lower than the tolerance concentration (25 ppm), and when the temperature was 870°C, CO was reduced to lower than the detection limit (25 ppm). At this time, the CO_2 in the gas at the outlet (11000 ppm) was nearly equal to the concentration of the CO introduced and H_2 was not detected, and accordingly it can be considered that CO has all been oxidized to CO_2.

Comparative Example 1A

The same experiment as in Example 1 was carried out with the use of the apparatus of Example 1 by introducing CO at a concentration of 1.33% and H_2O at a flow velocity of 0.079 mL/min at a total gas flow rate of 410 sccm into the inside of the heat oxidation vessel without the addition of O_2 at a temperature of the gas phase portion of the heat oxidation vessel of 870°C for 30 minutes of

treatment unit which in turn results in a combustion of particles in the exhaust gases which functions optimally. In particular, the invention provides that a gas flow can be treated for filtration and elimination of particles at a certain temperature with a low heat consumption. During heating of the gas flow, a certain amount of heat (for a given gas volume) is consumed, which later on can be recovered for heating a new inflowing gas volume. This results in a heat exchanging effect which requires considerably less consumption of energy than traditional heating systems which, for example, are based on separate heater elements, e.g. of the electric type.

In the embodiments of the invention which comprise coatings of catalytic material, the strip package 19b can be formed in such manner that it is coated with a catalytic material which provides a function which corresponds to a three-way catalyst, i.e. which is utilized for catalytic elimination of undesired compounds in the form of nitric oxides, carbon monoxide and hydrocarbon compounds in the exhaust gases from the engine 1. Techniques for coating surfaces with thin coatings of catalytic material are previously known e.g. when manufacturing conventional car catalysts. Moreover, the strip package 19b can be provided with a NO_x reducing coating, i.e. a coating which provides a function which corresponds to a nitrogen oxide adsorbent (also called NO_x adsorbent). According to what is previously known, a NO_x adsorbent can in a known manner be utilized for reduction of NO_x compounds in the exhaust gases of the engine 1.

Thus, the exhaust gas treatment unit 18 can constitute an integrated component which is utilized as particle filter and which also comprises both NO_x reducing material (which thus constitutes a so-called NO_x adsorbent) and, where appropriate, material which provides the function

the treating time. The results are set forth in Table 2.

As would be understood from Table 2, even when the temperature of the gas phase portion was 870°C, by the addition of H_2O alone, the removal ratio of CO was merely 38%, and thus the disposal performance of CO was low.

Comparative Example 1B

The same experiment as in Example 1 was carried out with the use of the apparatus of Example 1 by introducing CO at a concentration of 1.24% and O_2 at a concentration of 3.8% at a total gas flow rate of 410 sccm without the addition of H_2O at a temperature of the gas phase portion of the heat oxidation vessel of 870°C for 30 minutes of the treating time. The results are set forth in Table 2.

As would be understood from Table 2, even when the temperature of the gas phase portion was 870°C, the addition of O_2 alone could not completely remove CO, and 200 ppm of CO which greatly exceeded the tolerance concentration (25 ppm) were detected in the gas at the outlet.

Table 2

	Gas at Inlet			Gas at Outlet				Removal Ratio of CO (%)
	CO (%)	O_2 (%)	H_2O (mL/min)	CO (ppm)	CO_2 (ppm)	O_2 (%)	H_2 (ppm)	
Example 1 (870°C)	1.28	3.7	0.079	<2	11000	3.2	<2	100
Comparative Example 1A	1.33	0	0.079	8330	3220	<0.3	<2	38
Comparative Example 1B	1.24	3.8	0	200	11600	3.1	<2	98

Example 2

The disposal performance of the PFC exhaust gas treating apparatus according to the present invention was observed. As the PFC exhaust gas treating apparatus, an apparatus 10 having a structure shown in Fig. 1 was used. As the heat oxidation vessel 20 and the catalytic reaction vessel 30, stainless steel mini-columns having an inner

of a conventional three-way catalyst. In this manner, a combined effect against NO_x compounds and hydrocarbons as well as particles is provided. NO_x reduction is provided in the stoichiometric case by means of said three-way catalyst and in the lean case by means of the NO_x adsorbent.

The invention is not limited to said design as such an integrated unit which simultaneously functions as three-way catalyst and NO_x adsorbent, but may also be based on the fact that the exhaust gas treatment unit comprises for example NO_x adsorbing material and is connected to a separate unit in the form of a three-way catalyst. According to an additional alternative, the exhaust gas treatment unit can be formed without either a NO_x adsorbent or a three-way catalyst, wherein both these functions in that case can be provided by means of separate units along the engine's exhaust pipe. Whichever specific design is selected in the present application depends, for example, on how the space in the present vehicle can be utilized. Other factors which determine the selection of design are the demands for an acceptable heating effect, pressure loss and loss of heat and factors regarding the production and the cost.

According to an alternative embodiment, the engine 1 can be connected to a pre-catalyst (not shown) of the three-way type. Suitably, the pre-catalyst is provided with a comparatively low oxygen storage capacity and is provided upstream of the exhaust gas treatment unit 18 and preferably comparatively close to the exhaust manifold 16. In that case, such a pre-catalyst is particularly adapted for rapid heating during cold starts of the engine 1, i.e. so that its catalytic coating rapidly becomes active. This provides a considerable elimination of HC, CO, and NO_x compounds in the exhaust gases, particularly during low idle flows. Due to the fact that

diameter of 27 mm and a height of 500 mm were used. As the γ-alumina, "Neobead GB-08" (a product of Mizusawa Chemical Co., Ltd., Na_2O content of not greater than 0.01% by weight) having a particle diameter of 0.8 mm and a crystal structure which exhibits diffraction lines having an intensity of 100 or more at five angles of 33° ± 1°, 37° ± 1°, 40° ± 1°, 46° ± 1° and 67° ± 1° of the angles of diffraction 2θ measured by an X-ray diffraction apparatus was filled in the catalytic reaction vessel 30 to a height of 100 mm (a filled amount of 57 mL). As the heating means for the heat oxidation reaction vessel 20 and the catalytic reaction vessel 30, ceramic electric tubular furnaces 28 and 32 were used. Within these furnaces, the heat oxidation reaction vessel 20 and the catalytic reaction vessel 30 were mounted. The temperatures of the oxidation reaction zone 20b in the heat oxidation vessel 20 and the inside of the catalytic reaction vessel 30 were measured by thermocouples (not shown in the Figure) installed at their center portion.

The temperature of the oxidation reaction zone 20b in the heat oxidation reaction vessel 20 was heated to 870°C and that of γ-alumina in the catalytic reaction vessel 30 was heated to 750°C, and CO and CF_4 diluted with N_2 as an artificial test PFC exhaust gas and at least equimolar amounts of CO_2 an O_2 were introduced into the heat oxidation vessel 20 at a total gas flow rate of 410 sccm. The concentrations introduced were set at CO: 1.24%, CF_4: 1.61%, and O_2: 5.6%, respectively, and the flow velocity of H_2O was set at 0.079 mL/min.

In order to confirm the disposal performance of the present apparatus, concentration of CO, CF_4, CO_2, O_2 and H_2 in the gas at the outlets of the heat oxidation vessel and the catalytic reaction vessel were analyzed by a gas chromatograph apparatus equipped with a mass detector ("AGS-7000U", manufactured by Anelva Co., Ltd.). The results are set forth in Table 3.

Table 3

the flowing exhaust gases can be heated rapidly by means of the pre-catalyst, a comparatively rapid heating is also provided for the subsequent exhaust gas treatment unit 18, i.e. a comparatively short time that passes until the exhaust gas treatment unit 18 has been heated to a temperature at which it is capable of combusting the harmful particles which are separated by means of the strip package 19b. This results in an efficient exhaust purification for the engine 1, particularly during cold starts.

In some cases, e.g. for protecting the material in the exhaust gas treatment unit 18 from too high temperatures which can occur during some operating conditions, cooling of the unit may come into question. If so, the temperature can be reduced in a number of ways, e.g. by means of external cooling. More precisely, this could be implemented by supplying for example water or air, which in that ~~case is supplied through the exhaust gas~~ treatment unit 18. This is not shown in the drawings. An additional manner is to utilize (not shown) cooling flanges in the exhaust gas treatment unit 18. In that case, said cooling flanges can be controlled by means of bimetals, ~~which results in a system which can~~ be utilized for temperature control without the need to utilize the control unit 5.

An additional ~~possibility~~ of reducing the temperature in the exhaust gas ~~treatment unit 18 is to supply co~~ld air, for example from an (not ~~shown) air pump, into~~ the return chambers 24. Due to the effect of the interchange of heat which is obtained according to the invention, even small amounts of supplied air results in a considerable temperature reduction of the gas flow through the exhaust gas treatment unit 18.

Sampling Point	Gas at Outlet				
	CO(ppm)	CF_4(ppm)	CO_2(%)	O_2(%)	H_2(ppm)
At Outlet of Heat Oxidation Vessel	<1	15400	1.19	4.5	<2
At Outlet of Catalyst Reaction Vessel	<1	<1	2.79	3.9	55

As would be clear from Table 3, at the outlet of the heat oxidation vessel, CO was disposed to lower than the detection limit (2 ppm) but CF_4 was not removed. At the outlet of the catalytic reaction vessel, both CF_4 and CO were disposed to lower than the detection limit (1 ppm for CF_4 and 2 ppm for CO). Accordingly, it has been confirmed that the present apparatus which combines a heat oxidation vessel with a catalytic reaction vessel has enabled good treatment of both CO and CF_4.

Comparative Example 2

In order to observe the effect of treating CO without passing a PFC exhaust gas through the heat oxidation vessel, an artificial test exhaust gas and O_2 and H_2O were directly passed through the catalytic reaction vessel under the same conditions as in Example 2 excepting the heat oxidation vessel to carry out a comparative example. The results are set forth in Table 4.

Table 4

	Gas at Outlet of Catalyst Reaction Vessel				
	CO(ppm)	CF_4(ppm)	CO_2(%)	O_2(%)	H_2(ppm)
Example 2	<1	<1	2.79	3.9	55
Comparative Example 2	3700	<1	2.42	4.1	39

As would be clear from Table 4, although the disposal of CF_4 was possible only by the catalytic reaction vessel, CO removal ratio was as low as 70%, and CO could not be disposed to lower than the tolerance concentration.

From the above described Examples and Comparative

The supplied cold air can be non-compressed or compressed. According to one solution, the supplied air can be constituted by compressed air which is taken from the induction pipe of the engine, preferably after a (not shown) compressor forming part of a (not shown) turbo-aggregate. Alternatively, the cold air can be constituted by exhaust gases which are guided out from the exhaust manifold of the engine (before the turbo-aggregate) and which are cooled down (e.g. by means of a suitable form of after-treatment).

The main principle for external cooling is to carry off heat from the return chambers 27, 28 essentially without any mass exchange. During air injection, the heat that is present will be "diluted" and the temperature drops by means of supply of cold gas into the flow. In both cases, the principle of exchange of heat functions as a step-up exchange and results in a considerable enhanced effect as regards the temperature.

By means of an arrangement of the above-mentioned kind, an effective control of the temperature of the gas flow is obtained, so that said gas flow can be controlled and adjusted to a value which is optimally adjusted to the prevailing operating condition. This is particularly achieved by means of the fact that the design of the exhaust gas treatment unit 18 provides a satisfying heat transmission and a catalytic effect by means of a satisfying contact between the flowing gas and the walls in the exhaust gas treatment unit 18.

In order to facilitate the temperature control of the invention, the invention can comprise a (not shown) temperature sensor which is provided in connection with the exhaust gas treatment unit 18. In that case, such a temperature sensor can be connected to the control unit 5 via an electrical connection and deliver a measurement

Examples, it could be understood that the use of the gas treating apparatus according to the present invention which comprises a heat oxidation vessel and a γ-alumina-filled catalytic reaction vessel enables efficient treatment of a gas containing CO and fluorine-containing compounds.

According to the present invention, a gas containing fluorine-containing compounds and CO can be disposed to carry out oxidation of CO and decomposition of the fluorine-containing compounds efficiently and simultaneously, whereby the running cost becomes low and effective treatment becomes possible.

According to the present invention, treatment with each different catalyst, heating vessels to fill different catalysts, control of the treating temperature for each heating vessel and a wide space for installing apparatuses are not needed in treating a gas containing fluorine-containing compounds and CO, and the temperature control is rendered easy.

Further, since the use of different catalysts each having a different life is not required, the control of the catalyst is rendered easy. Furthermore, no specific catalyst for removing CO is necessary, and thus the running cost such as the expense in an periodical exchange of the catalyst can be lowered.

value which corresponds to the prevailing temperature of the exhaust gas treatment unit 18. In that case, said measurement value can be utilized during the control of an increase and a reduction, respectively, of the temperature of the exhaust gas treatment unit 18, according to the methods which in turn have been explained above. In this manner, an accurate control of the temperature of the exhaust gas flow is provided. It is in particular suitable to utilize information regarding the temperature in the respective return chamber 27, 28, but information regarding the temperature in other parts of the exhaust gas treatment unit 18 may also be of interest. In such a case, more than one temperature sensor can be utilized for determinating the temperature in a corresponding number of points.

However, it shall be emphasized that the invention is not limited to merely the type of system which comprises such a separate temperature sensor, but the invention can also be realized by letting the control unit 5 comprise a program with a calculation model which predicts the temperature of the exhaust gas treatment unit 18 during various operating conditions with a satisfying accuracy.

The invention can be formed in order to prevent clogging of carbon and similar particles, i.e. in order to provide a high degree of filtration even after some time of use. This can be obtained by means of optimization of various parameters, e.g. the geometric design of the exhaust gas treatment unit 18, i.e. its length, width and height. Furthermore, the form and wave height of the corrugations 20 - as well as the distance between two adjacent corrugations - can be adjusted in order to prevent such clogging. In this regard, the control of the engine 1 can also be optimized.

WHAT IS CLAIMED IS:

1. A process for treating a gas containing fluorine-containing compounds and CO which comprises contacting the above described gas with O_2 and H_2O at a temperature of 850°C or higher to oxidize the CO to CO_2; and then contacting the gas with γ-alumina at a temperature of 600-900°C to decompose the fluorine-containing compounds.

2. The process of claim 1, wherein the γ-alumina has a crystal structure which exhibits diffraction lines having an intensity of 100 or more at five angles of 33° ± 1°, 37° ± 1°, 40° ± 1°, 46° ± 1° and 67° ± 1° of the angles of diffraction 2θ measured by an X-ray diffraction apparatus.

3. An apparatus for treating a gas containing fluorine-containing compounds and CO which comprises a heat oxidation vessel having a hollow inside enabling the passage of the above described gas therethrough, a heating means capable of heating the temperature of the gas in the hollow inside to 850°C or higher, a gas inlet, an O_2 inlet and H_2O inlet; and a catalytic reaction vessel which is under fluid-communicating condition with the heat oxidation vessel and has been filled with γ-alumina.

4. The apparatus of claim 3, wherein the catalytic reaction vessel further has a heating means capable of heating the γ-alumina to 600 to 900°C.

5. The apparatus of claim 3, wherein the γ-alumina has a crystal structure which exhibits diffraction lines having an intensity of 100 or more at five angles of 33° ± 1°, 37° ± 1°, 40° ± 1°, 46° ± 1° and 67° ± 1° of the angles of diffraction 2θ measured by an X-ray diffraction apparatus.

6. The apparatus of claim 3, wherein the heat oxidation vessel further has a contact auxiliary means for enhancing the contact efficiency of the CO in the gas with O_2 and H_2O.

7. The apparatus of claim 4, wherein the heat oxidation vessel further has a contact auxiliary means for enhancing the contact efficiency of the CO in the gas with O_2 and H_2O.

8. The apparatus of claim 5, wherein the heat oxidation vessel further has a contact auxiliary means for enhancing

Furthermore, the invention can be optimized in order to provide a lowest possible pressure loss. This can take place by means of an adjustment of the geometric construction of the exhaust gas treatment unit 18, i.e. its length, width and height.

The invention is not limited to the embodiment which is described above and shown in the drawings, but may be varied within the scope of the appended claims. For example, the strip 19a can be manufactured by a thin metal plate or foil, e.g. by rustless steel. This metal plate ~~or foil can be coated with the above-mentioned catalytic material~~. Alternatively, ~~the strip 19a~~ can consist of a ceramic material which in that case has been impregnated or coated with the catalytic material. Furthermore, the material can alternatively be manufactured in the form of thin sheets or similar elements, which in that case are arranged in a package and subsequently are joined together along the edges so that the above-mentioned strip package 19a is formed.

If the exhaust gas treatment unit 18 comprises materials which provide the function of a three-way catalyst and a NO_x adsorbent, respectively, these materials can be arranged in various ways. For example, said materials can be situated on various areas along the exhaust gas treatment unit 18. For example, the inlet part of the exhaust gas treatment unit 18 can function as a three-way catalyst whereas the inner parts of the exhaust gas treatment unit 18 functions as a NO_x adsorbent. In that case, by means of a suitable design, the above-mentioned pre-catalyst 32 can also be eliminated.

The inlet and the outlet, respectively, of the exhaust gas treatment unit 18 can be positioned according to what has been explained above, i.e. essentially centrally on the respective side wall 24c, 24d. Alternatively, it is

the contact efficiency of the CO in the gas with O_2 and H_2O.

possible to position the inlet and the outlet displaced towards either direction along the respective side wall. For example, this displacement can be of such a distance that the inlet will be situated right up in one end of the strip package. In such a case, only one return chamber is utilized.

The invention is not limited for utilization in connection with merely diesel engines, but can in principle be applied in all types of combustion processes where particles in the form of, for example, carbon are present in the exhaust gases from engines which at least periodically are operated by a surplus of oxygen.

Generally, the invention is not limited for utilization in connection with motor vehicles, but may be applied in other connections where there is a demand for filtering particles in a gas flow.

PROCESS AND APPARATUS FOR TREATING GAS CONTAINING FLUORINE-CONTAINING COMPOUNDS AND CO.

ABSTRACT OF THE DISCLOSURE

The purpose of the present invention is to provide a process and an apparatus for efficiently treating a gas containing fluorine-containing compounds and CO to be discharged, for example, from the step of dry cleaning the inner surfaces and the like of a semiconductor manufacturing apparatus or the step of etching various types of formed films such as oxide films in the semiconductor industry. In order to accomplish the above-mentioned purpose, the gas treating process according to the present invention is a process for treating a gas containing fluorine-containing compounds and CO which comprises contacting the above described gas with O_2 and H_2O at a temperature of 850°C or higher to oxidize the CO to CO_2; and then contacting the gas with γ-alumina at a temperature of 600 to 900°C to decompose the fluorine-containing compounds.

CLAIMS:

1. Method for treatment of a gas flow, comprising:

guiding the gas flow through a gas treatment unit (18) adapted for filtering particles in said gas flow, and

eliminating said particles in said gas treatment unit (18),

c h a r a c t e r i z e d i n that it comprises:

filtering particles in said gas flow by accumulating said particles in, or in connection with, a number of ducts (21) forming part of the gas treatment unit (21) during passage of the gas flow through the gas treatment unit (18),

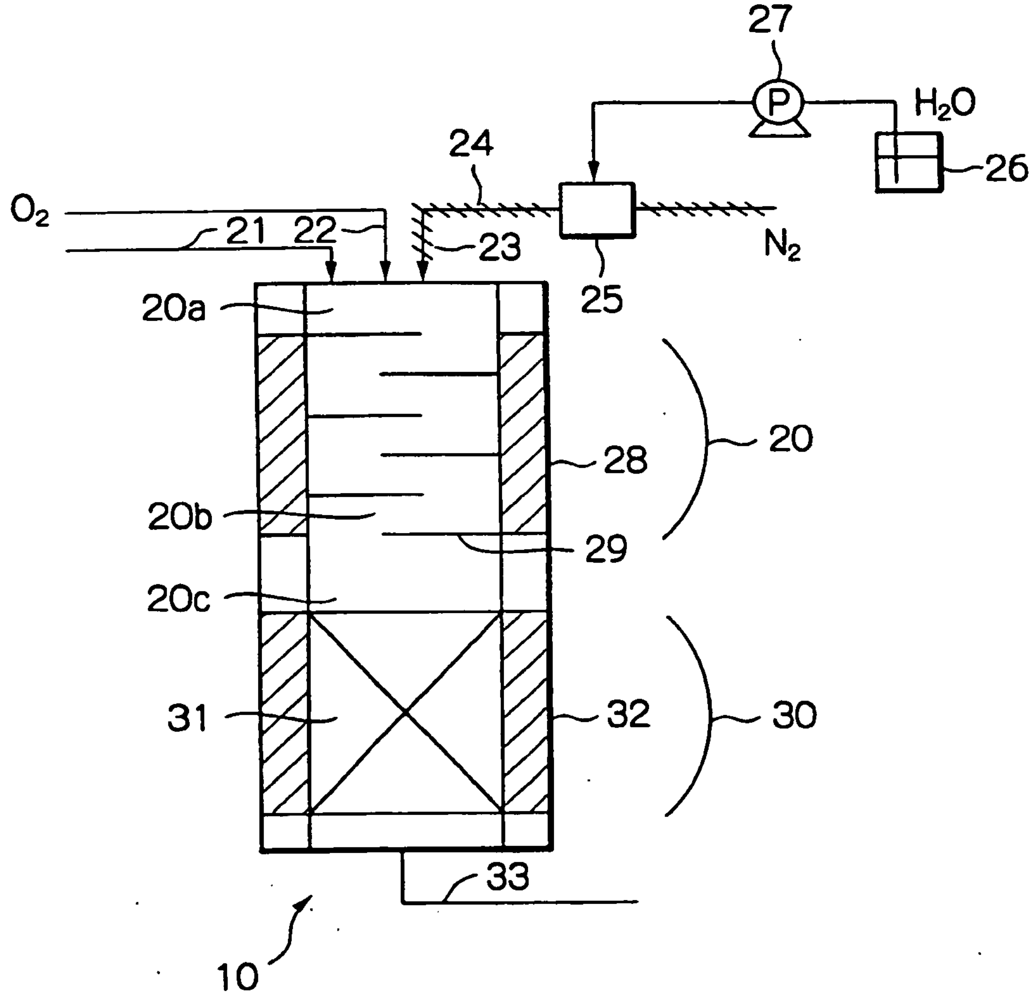
controlling the temperature of said gas flow along said ducts (21) to a value which provides combustion of said particles, and

eliminating said filtered particles in said gas treatment unit (18) by means of combustion in said ducts (21).

2. Method according to claim 1, c h a r a c t e r i z e d i n that said temperature control of said gas flow takes part by means of exchange of heat between the ducts (21), wherein the ducts (21) are connected to an inlet and an outlet, respectively, of the gas treatment unit (18) so that the gas flow takes part during exchange of heat between incoming and outgoing flows of said gas flow.

3. Method according to claim 1 or 2, wherein said gas flow is constituted by a flow of exhaust gases from a combustion engine (1),

Fig. 1



c h a r a c t e r i z e d i n that said temperature control of said gas flow takes place by means of at least one of the following measures:

i) controlling the injection time and the ignition sequence of said engine (1) so that an increased gas temperature is obtained,

ii) controlling said engine (1) wherein additional injection of fuel is made during the exhaust stroke of the engine,

iii) controlling said engine (1) periodically between rich and lean operation,

iv) injecting air from an external source and into the exhaust gas treatment unit (18) during rich operation of the engine (1),

v) controlling the cylinders individually, wherein the exhaust gases from one or some of the cylinders of the engine (1) are operated in a rich manner whereas the remaining cylinders are operated in a lean or stoichiometric manner,

vi) supplying heat through a heater element (31) which is provided in the exhaust gas treatment unit (18),

vii) injecting fuel in the exhaust gases after the engine (1),

viii) oxidizing uncombusted hydrocarbons in said exhaust gas treatment unit (18).

4. Method according to any of the preceding claims, c h a r a c t e r i z e d i n that said filtering is made by means of surface filtering in said exhaust gas treatment unit (18).

5. Method according to any of claims 1-3, c h a r a c t e r i z e d i n that said filtering is made by means of deep filtering in said exhaust gas treatment unit (18).

6. Method according to any of claims 1-3, c h a r a c t e r i z e d i n that said filtering is made by means of an electric filter, wherein said accumulation of particles takes place on an earthed element in said exhaust gas treatment unit (18).

7. Method according to any of claims 1-6, c h a r a c t e r i z e d i n that said filtering is made during turbulent flow of said gas, for mixture of said gas.

8. Method according to any of the preceding claims, c h a r a c t e r i z e d i n that it comprises reducing undesired emissions in said gas flow by means of a catalytic coating in said ducts (21).

9. Method according to claim 8, c h a r a c t e r i z e d i n that it comprises reducing NO_x compounds in said gas flow by means of said catalytic coating.

10. Method according to any of the preceding claims, c h a r a c t e r i z e d i n that it comprises determinating a measure regarding the temperature of said exhaust gas treatment unit (18) by means of at least one separate temperature sensor which is provided in connection with the exhaust gas treatment unit (18), wherein said measure is utilized during said control of the temperature.

11. Method according to any of claims 1-9, c h a r a c t e r i z e d i n that it comprises determinating a measure regarding the temperature of said exhaust gas treatment unit (18) by means of calculation models which are defined beforehand and which define a relationship between said temperature and the prevailing operating condition of the engine (1), wherein said

APPARATUS AND METHOD FOR PRETREATING EFFLUENT GASES IN A WET ENVIRONMENT

FIELD OF THE INVENTION

[0001] The present invention relates to an effluent gas treatment, and more particularly, to an apparatus and a method for pre-treating effluent gases from a semiconductor or LCD device manufacturing process in a wet environment.

BACKGROUND OF THE INVENTION

[0002] The effluent gases from semiconductor and LCD device manufacturing processes, such as low pressure chemical vapor deposition, plasma enhanced chemical vapor deposition and plasma etch, may contain toxic, corrosive or explosive gases, such as silane SiH_4, arsine AsH_3, phospine PH_3, diborane B_2H_6, tetraethoxysilan (TEOS) $Si(OC_2H_5)_4$, ammonia NH_3, boron trichloride BCl_3, chlorine Cl_2, sulfur hexafluoride SF_6, hexa-fluoro ethane C_2F_6 and carbon tetra-fluoride CF_4. Therefore, the effluent gases from these manufacturing processes must be properly treated, before they are released into the open atmosphere.

[0003] Particularly, perfluoro-compound (hereinafter "PFC") gases such as C_2F_6 and CF_4, which are used to clean a CVD process chamber, are known to make significant contributions to global warming because they absorb infrared light and remain in the atmosphere for an extended period of time. Therefore, the reduction of PFC gas emissions is an issue in the semiconductor and LCD industries. In order to address this issue, another PFC gas, NF_3, was introduced as an alternative for CVD chamber cleaning applications.

measure is utilized during said control of the temperature.

12. Method according to any of the preceding claims, c h a r a c t e r i z e d i n that said control of the temperature of said gas flow takes place by means of a particular control of the composition of said gas flow.

13. Device for treatment of a gas flow, comprising a gas treatment unit (18) adapted for filtering particles in said gas flow and for eliminating said particles, c h a r a c t e r i z e d i n that said gas treatment unit (18) is provided with a number of ducts (21) for filtering by means of accumulation of said particles in said ducts (21) during passage of the gas flow through the gas treatment unit (18), and that the gas treatment unit (18) is adapted for controlling the temperature of said gas flow to a value which provides combustion of said particles along said ducts (21).

14. Device according to claim 13, c h a r a c t e r i z e d i n that the ducts (21) are connected to an inlet and an outlet, respectively, of the gas treatment unit (18) so that the gas flow takes place during interchange of heat between incoming and outgoing flows of said gas flow.

15. Device according to any of claims 13 or 14, c h a r a c t e r i z e d i n that said exhaust gas treatment unit (18) is adapted for surface filtering of particles.

16. Device according to any of claims 13 or 14, c h a r a c t e r i z e d i n that said exhaust gas treatment unit (18) comprises a structure for deep filtering of particles.

[0004] NF_3 has higher utilization efficiency in cleaning the process chamber than the other PFC gases mentioned above, and rarely generates PFC by-products during the cleaning. Since a method called remote NF_3 chamber cleaning method is known to increase the utilization efficiency of NF_3 and reduce PFC gas emissions, NF_3 has drawn a lot of attention in the semiconductor and LCD industries. However, considering the rapid growth of the semiconductor and LCD industries, the amount of NF_3 used in the cleaning of the CVD chamber is expected to significantly increase, and the proper treatment of NF_3 will become a critical issue. Since NF_3 itself has high utilization efficiency and decompose almost entirely, the solution to this issue lies in treating the corrosive gases, such as F or F_2, generated by the decomposition of NF_3.

[0005] The methods that can be used to solve this problem may be classified into three categories: a wet method in which water-soluble components contained in the effluent gases are removed by dissolving the water-soluble components with water; a burning method in which inflammable components of the effluent gas are treated by decomposing or burning them at high temperatures; and an adsorption method in which components that do not burn or are not water-soluble are removed by chemically or physically adsorbing those components through adsorbents. Commercially available systems for treating effluent gases usually employ the combination of the burning method and either the wet method or the adsorption method in view of the safety and cost, rather than employ only one method out of the three methods mentioned above. Particularly, effluent gas treatment systems employing the combined method of the wet method and the burning method (hereinafter "burning-wet treatment system") are widely used to treat effluent gases.

[0006] In the burning-wet treatment system, the effluent gas goes through a burning treatment and subsequent wet treatment. The burning treatment burns the inflammable components contained in the effluent gas. The wet treatment separates

17. Device according to any of claims 13 or 14, c h a r a c t e r i z e d i n that said exhaust gas treatment unit (18) comprises en electric filter for ionization of said particles, and an earthed element in said exhaust gas treatment unit (18) for eliminating said particles.

18. Device according to any of claims 13-17, c h a r a c t e r i z e d i n that the gas treatment unit (18) is adapted for generating a turbulent flow for mixing said gas.

19. Device according to any of claims 13-18, c h a r a c t e r i z e d i n that the exhaust gas treatment unit (18) comprises a catalytic coating in said ducts (21) for reducing undesired emissions in said gas flow.

20. Device according to any of claims 13-19, c h a r a c t e r i z e d i n that it comprises at least one temperature sensor which is provided in connection with the exhaust gas treatment unit (18), for determinating the temperature of said exhaust gas treatment unit (18).

21. Device according to any of claims 13-20, c h a r a c t e r i z e d i n that said exhaust gas treatment unit (18) comprises a strip (19a) which is folded into a package (19b), by means of which said ducts (21) are formed.

the silicon oxide powder produced during the burning treatment and removes the water-soluble components of the effluent gas by spraying water onto the effluent gas.

[0007] However, the burning-wet treatment system still has the problems of powder clogging and corrosion, like other types of effluent gas treatment systems. That is, when the effluent gas discharged from the CVD chamber is introduced into the effluent gas treatment system, fine powder contained in the effluent gas gradually adsorbs onto the walls of the chamber for burning treatment, the exhaustion pipe or duct, which results in powder clogging. The powder clogging necessitates frequent maintenance of the effluent gas treatment system. Moreover, corrosive gases, such as F or F_2, contained in the effluent gas easily stick to the walls of the exhaustion pipe or duct and erode the walls, which shortens the life span of the effluent gas treatment system. The increase in maintenance and reduction of the life span of the effluent gas treatment system directly affect the manufacturing costs of semiconductor or LCD devices.

[0008] In order to solve these problems, a wet pre-treatment system has been introduced that removes the corrosive gas or fine powder contained in the effluent gas before the effluent gas enters the effluent gas treatment system. Effluent gas treatment systems employing a wet pre-treatment unit are disclosed in USP 5,955,037 to Mark Holst et al. and USP 5,649,855 to Hiroshi Imamura. USP 5,955,037 relates to an effluent gas treatment system that includes a wet pretreatment unit for removing the fine particulates and acidic gas contained in the effluent gas before the effluent gas is introduced into an oxidation chamber. The wet pre-treatment unit disclosed in USP 5,955,037 comprises a wet spray tower, which separates and removes the particulates by adsorbing the fine powder of the effluent gas onto water droplets or water vapor to facilitate the agglomeration of the particulates. In detail, water droplets are downwardly introduced into the spray tower through a spray nozzle provided at the upper portion of the spray tower, while the effluent gas is upwardly introduced into the

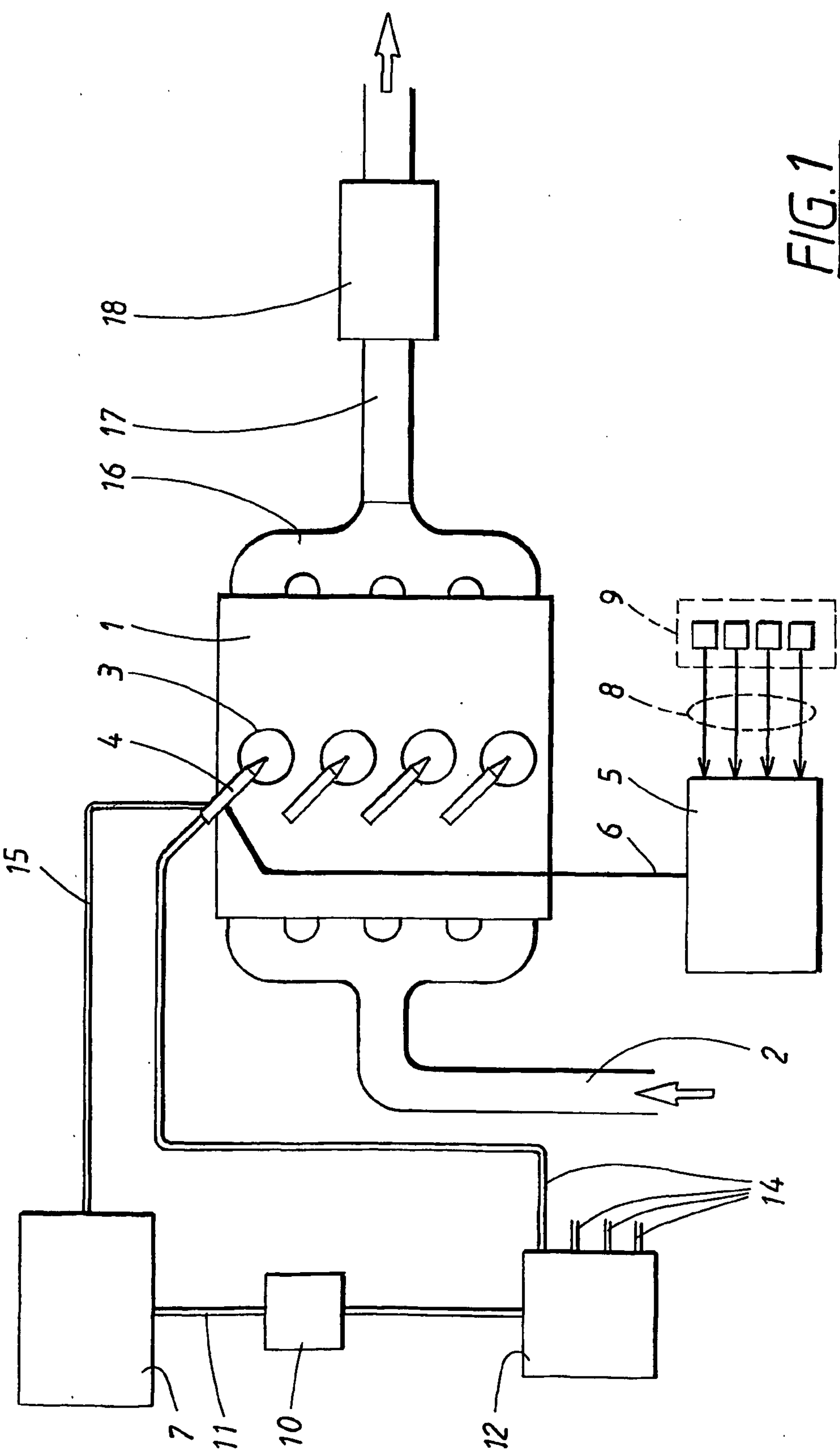


FIG.1

spray tower through an inlet provided at the lower portion of the spray tower. The effluent gas flowing upward in the wet spray tower counter-currently contacts the water droplets to effect initial abatement of fine powder and the acidic gas. Although the wet spray tower is cheap to install and maintain, easy to fix, and has little pressure loss, the short contact time between the water droplets and the effluent gas is problematic to effect a sufficient abatement of fine powder and corrosive gas.

[0009] USP 5,649,985 relates to a method for effectively removing the harmful substances of exhaust gas discharged during a semiconductor device manufacturing process, and discloses a water scrubber, located upstream of a thermal decomposition unit, for removing at least one of the water-soluble components, hydrolysable components and dust contained in the exhaust gas by water-scrubbing. Especially, USP 5,649,985 describes a water scrubber composed of a spray tower and a venturi. The venturi has an upwardly flared portion, a throat portion and a downwardly flared skirt portion. The exhaust gas introduced into the flared portion of the venturi is pre-treated with high-pressure water mist sprayed from the spray nozzle provided on a ceiling of the flared portion. Since the high-pressure water mist is compressed into a high-speed flow in the throat portion, and the water mist and the effluent gas flow in the same direction, highly effective contact between the water and the effluent gas can be achieved.

[0010] The contact between the water mist and the effluent gas removes the water-soluble components and hydrolysable components and dust from the effluent gas by dissolution or hydrolysis. Although the composite water scrubber disclosed in USP 5,649,985 can achieve high treatment efficiency, the pressure drop at the throat due to the fast flow of the water and the effluent gas is a problem. The pressure drop in the water scrubber hinders the effluent gas, thermally decomposed at the downstream oxidation chamber, from discharging out of the oxidation chamber. In order to easily

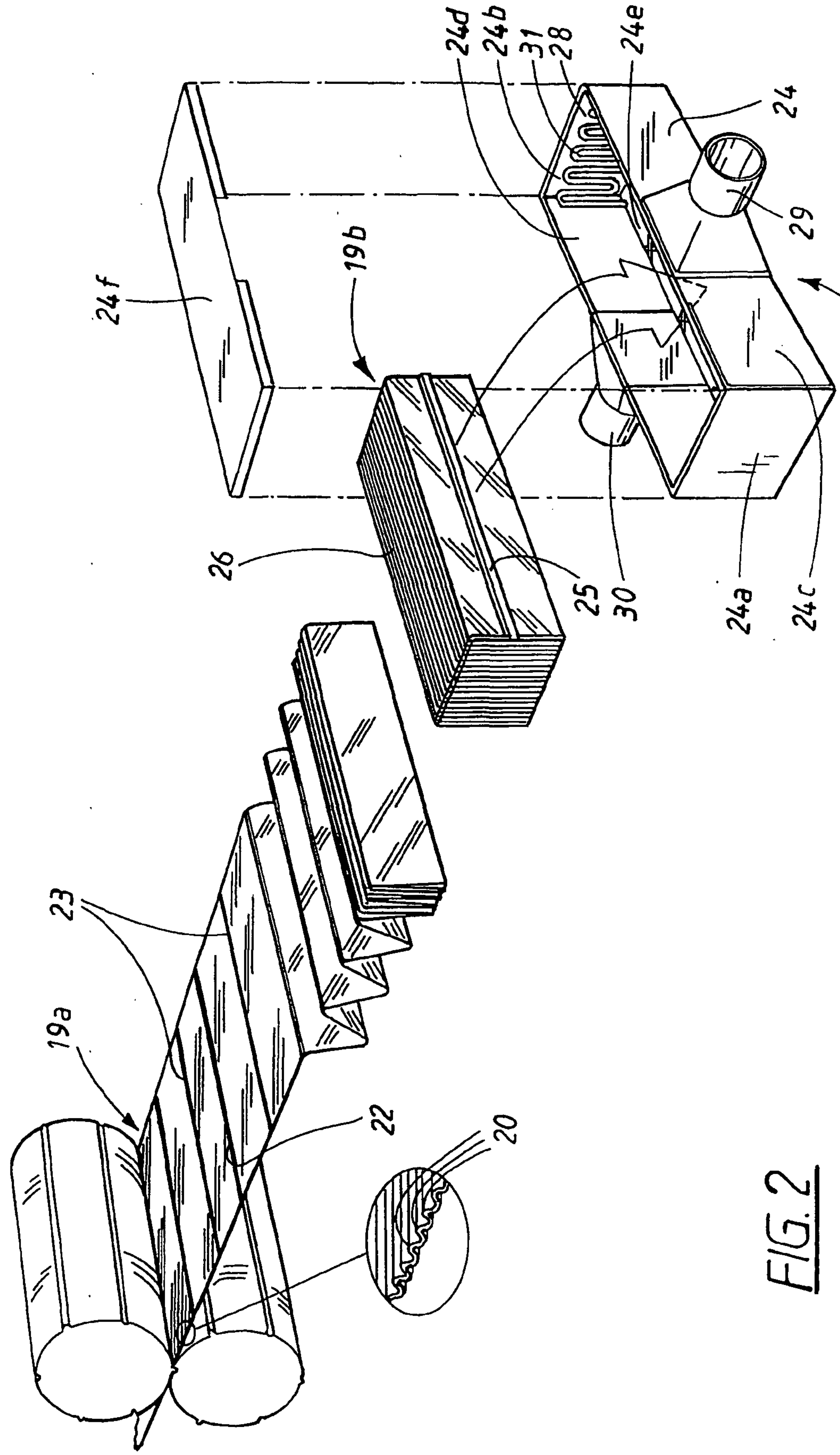


FIG.2

exhaust the thermally decomposed gas out of the oxidation chamber, the effluent gas treatment system disclosed in USP 5,649,985 also comprises an exhaust fan. However, the addition of the exhaust fan increases the manufacturing cost of the effluent gas treatment system.

SUMMARY OF THE INVENTION

[0011] Therefore, an objective of the present invention is to provide a wet pre-treatment apparatus for inexpensively and efficiently pre-treating effluent gases from semiconductor or LCD device manufacturing processes.

[0012] Another objective of the present invention is to provide a wet pre-treatment apparatus for removing water-soluble components contained in the effluent gases, thereby reducing the treatment burden of the effluent gas treatment system.

[0013] Still another objective of the present invention is to provide a wet pre-treatment apparatus for removing fine powder produced in the semiconductor or LCD device manufacturing processes, thereby preventing the powder clogging in the effluent gas treatment system.

[0014] Still another objective of the present invention is to provide a wet pre-treatment apparatus for removing corrosive substance such as F_2 generated during the cleaning of a CVD chamber, thereby minimizing corrosion of the effluent gas treatment system.

[0015] Still another objective of the present invention is to provide a method for pre-treating water-soluble components and fine powder contained in the effluent gas using a wet pre-treatment apparatus employing cyclone effect.

[0016] In accordance with one aspect of the present invention, an apparatus for pre-treating an effluent gas in a wet environment upstream of an effluent gas treatment system is provided which comprises an atomizer for atomizing a reagent, and a

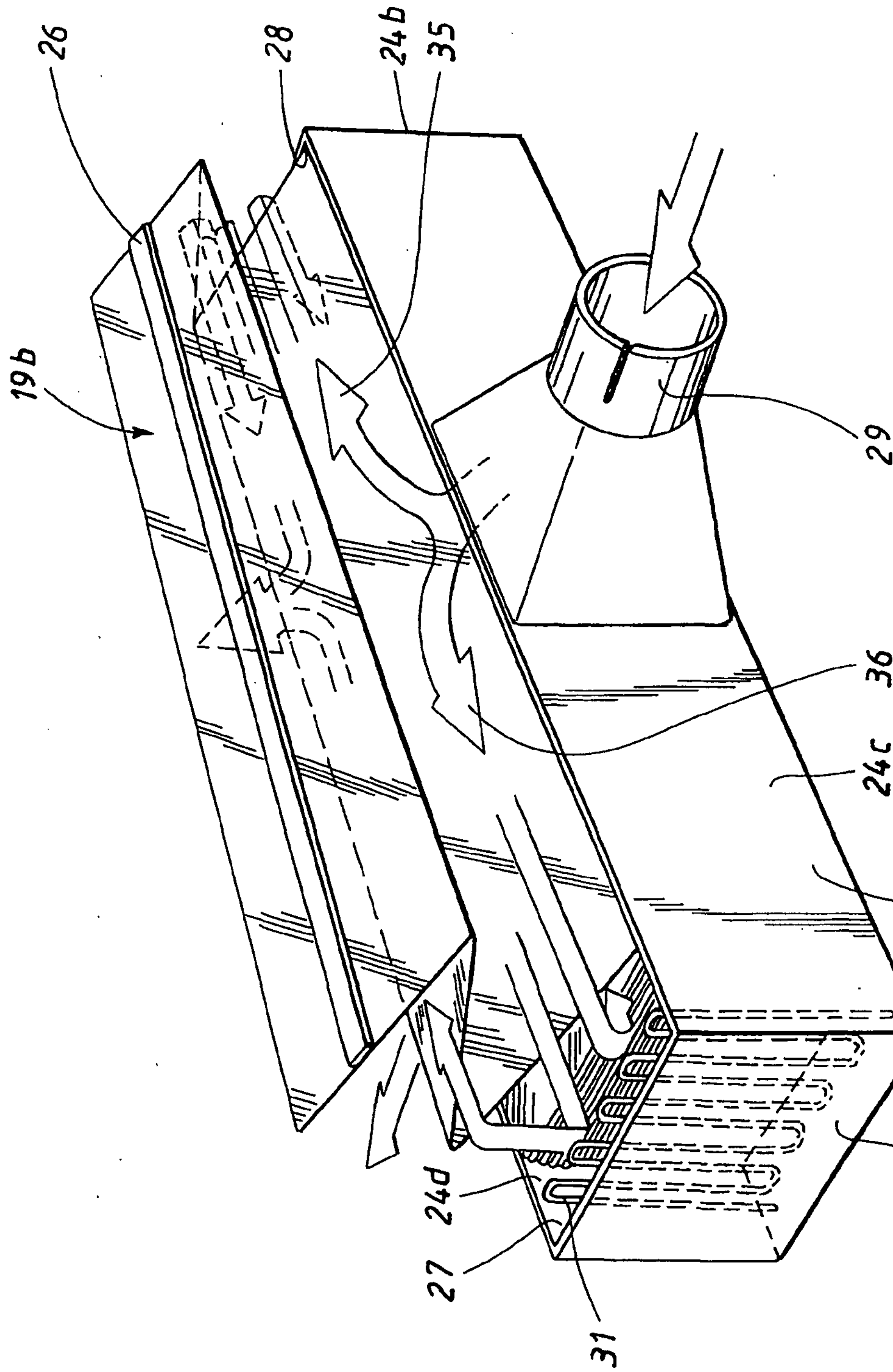


FIG.3

processing section comprising an inner tubular member and an outer tubular member. The processing section includes an effluent gas inlet for introducing the effluent gas into the processing section and an atomized reagent inlet for introducing the atomized reagent into the processing section. The effluent gas is pre-treated by the atomized reagent within the processing section. The processing section further includes an effluent gas outlet for discharging the effluent gas pre-treated by with the atomized reagent and a waste liquid outlet for discharging a waste liquid produced by the pre-treatment.

[0017] In accordance with another aspect of the present invention, a multi-unit wet pre-treatment apparatus comprising a plurality of wet pre-treatment units is provided to pre-treat effluent gas streams from a plurality of process chambers of semiconductor or LCD manufacturing tools.

[0018] In accordance with still another aspect of the present invention, a method for pre-treating an effluent gas in a wet environment before the effluent gas enters an effluent gas treatment system is provided which comprises the steps of introducing the effluent gas into a processing section; introducing an atomized reagent into the processing section; pre-treating the effluent gas with the atomized reagent in the processing section by using cyclone effect to produce a pre-treated effluent gas and a waste liquid; discharging the pre-treated effluent gas through an effluent gas outlet; and discharging the waste liquid through a waste liquid outlet.

BRIEF DESCRIPTION OF DRAWINGS

[0019] The above and other objects and features of the present invention will become apparent from the following description of the embodiments given in conjunction with the accompanying drawings.

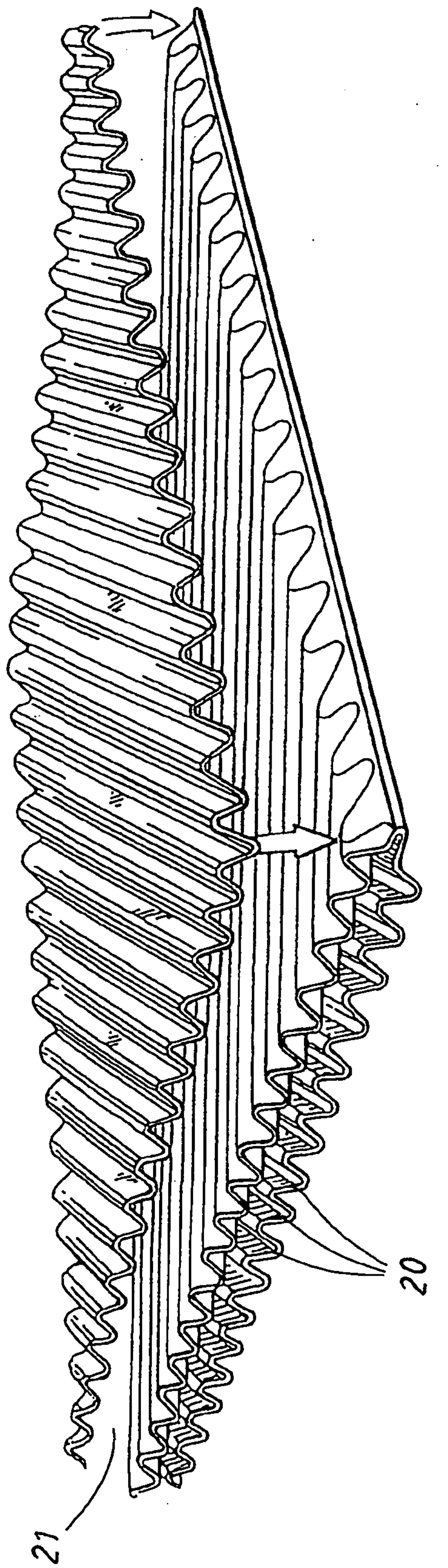


FIG. 4

Fig. 1 is a schematic diagram of a wet pre-treatment apparatus in accordance with an embodiment of the present invention.

Fig. 2 is a schematic diagram of a wet pre-treatment apparatus in accordance with another embodiment of the present invention.

Fig. 3 is a schematic diagram of a multi-unit wet pre-treatment apparatus in accordance with another embodiment of the present invention.

Fig. 4 illustrates test results on ammonia removal efficiency of the wet pre-treatment method in accordance with the present invention.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0020] Referring to Fig. 1, wet pre-treatment apparatus 10 of the present invention comprises processing section 20 designed to pre-treat the effluent gas using a cyclone effect and atomizing spray nozzle 15. Wet pre-treatment apparatus 10 of the present invention is constructed to have effluent gas inlet 11, reagent inlet 12, effluent gas outlet 21 for discharging the wet pre-treated effluent gas and waste liquid outlet 31 for draining waste water containing the fine powder and water-soluble components removed from the effluent gas.

[0021] Processing section 20 of wet pre-treatment apparatus 10 utilizes a cyclone effect where the centrifugal force of swirling fluids separates solid particulates or liquid droplets dispersed in the fluids. Water-soluble constituents and fine powder are separated from the effluent gas by spraying the reagent onto the effluent gas swirling inside processing section 20. Processing section 20 comprises inner tubular member 19 and outer tubular member 10a, where outer tubular member 10a has upper cylindrical portion 17 and lower conical portion 18. Thus, processing section 20 of wet pre-treatment apparatus 10 has the general shape of an upside bottle down.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 01/02135

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: F01N 3/023

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, PAJ, EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0668437 A1 (FIRMA J. EBERSPÄCHER), 23 August 1995 (23.08.95), column 1, line 13 - line 39; column 6, line 36 - column 7, line 31, figures 1,3, abstract --	1-20
X	WO 9604509 A1 (HEED, BJÖRN), 15 February 1996 (15.02.96), figures 1-3, abstract --	13-21
X	EP 0504719 A1 (SCHWÄBISCHE HÜTTENWERKE GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG), 23 Sept 1992 (23.09.92), column 1, line 45 - line 55; column 6, line 43 - line 53, figures 1-2, abstract --	1-20

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search	Date of mailing of the international search report
9 January 2002	21-01-2002
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Johan Westerbergh/ELY Telephone No. +46 8 782 25 00

Connector 17a provided at the top of upper cylindrical portion 17 connects inner tubular member 19 and outer tubular member 10a. Waste liquid outlet 31 is installed at the bottom of lower conical portion 18. The length of outer tubular member10a increases the contact time between the effluent gas and the reagent. However, the length of outer tubular member 10a must be adjusted to maximize the cyclone effect.

[0022] Inner tubular member 19 has the general shape of a funnel, comprised of an upper cylindrical portion, a tapering portion following the upper cylindrical portion and a lower cylindrical portion following the tapering portion. Effluent gas outlet 21 is installed at the top of inner tubular member 19. Connector 19a for connecting inner tubular member 19 and outer tubular member 10a is provided right below the tapering portion of inner tubular member 19. Inner tubular member 19 extends to the lower end of upper cylindrical portion 17 of outer tubular member 10a so that even when the reagent is sprayed widely in the longitudinal direction by atomizing spray nozzle 15, the pre-treated effluent gas does not contact the reagent again before being discharged through effluent gas outlet 21. By interconnecting connector 17a and connector 19a, inner tubular member 19 and outer tubular member 10a are interconnected. The interconnection is made with, for example, a clamp to allow an easy maintenance of the wet pre-treatment apparatus in case of powder clogging. A part of inner tubular member 19 projected into outer tubular member 10a is shown by the broken lines in Fig. 1, and the detailed structure of the interconnection is not shown in the drawings for clarity.

[0023] Effluent gas inlet 11 for introducing the effluent gas discharged from an upstream main chamber for CVD is installed at the outer wall of upper cylindrical portion 17 of outer tubular member 10a. Effluent gas inlet 11 is constructed so that the effluent gas is introduced perpendicular to the normal direction of upper cylindrical portion 17 of outer tubular member, i.e., tangential to the outer wall of upper

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4671059 A (ALEXANDER LAWSON), 9 June 1987 (09.06.87), figure 1, abstract --	1
A	WO 9627078 A1 (AB VOLVO), 6 Sept 1996 (06.09.96), page 6, line 27 - line 36 --	7,18
A	WO 9116529 A1 (AB VOLVO), 31 October 1991 (31.10.91), abstract -- --------	12

cylindrical portion 17 of outer tubular member 10a. Effluent gas inlet 11 and reagent inlet 12 are constructed so that the effluent gas and the reagent flow concurrently inside processing section 20, which would maximize the cyclone effect by allowing the effluent gas and the reagent to rotate in the same direction. Reagent inlet 12 is arranged above effluent gas inlet 11 to improve the pre-treatment efficiency of the effluent gas.

[0024] Atomizing spraying nozzle 15 for atomizing the reagent in order to increase the pre-treatment efficiency is installed at reagent inlet 12. Two inlet pipes 13 and 14, one for a gas and the other for the reagent, are connected to atomizing spray nozzle 15 in a direct compressing way. The inlet pipes are respectively provided with valves 13a and 14a to control the flow of the gas and reagent. The distal end of nozzle 15 extends into reagent inlet 12 so that atomized reagent 16 is sprayed into processing section 20 to react with the effluent gas.

[0025] Dehumidifier 23 is installed above effluent gas outlet 21 arranged at the top of inner tubular member 19 of processing section 20. Dehumidifier 23 and inner tubular member 19 of processing section 20 are connected by coupling effluent gas outlet 21 with dehumidifier inlet 22. Coupling effluent gas outlet 21 and dehumidifier inlet 22 with a clamp is preferable. Dehumidifier 23 is a cylindrical pipe interconnecting effluent gas outlet 21 of wet pre-treatment apparatus 10 and the effluent gas treatment system (not shown), the outer wall of which is uniformly heated by heater 24. Compressed gas provider 25 is installed at dehumidifier 23 to introduce compressed gas into dehumidifier 23. Compressed gas provider 25 is preferably arranged so that the compressed gas injected into dehumidifier 23 reaches an inlet of the effluent gas treatment system. Compressed gas provider 25 includes gas pipe 26 and valve 26a interlocked therewith. The inlet of the effluent gas treatment system, the effluent gas treatment system and a reservoir are not illustrated in the drawings for clarity.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SE 01/02135

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
EP	0668437	A1	23/08/95	DE	4405045	A,C	07/09/95
WO	9604509	A1	15/02/96	AT	195584	T	15/09/00
				AU	3088595	A	04/03/96
				CA	2196196	A	15/02/96
				DE	69518425	D,T	08/02/01
				EP	0774099	A,B	21/05/97
				SE	0774099	T3	
				ES	2149368	T	01/11/00
				JP	10504884	T	12/05/98
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				AT	129314	T	15/11/95
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WO	9627078	A1	06/09/96	AU	2760595	A	15/01/96
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				SE	466068	B,C	09/12/91
				SE	9001483	A	26/10/91

[0026] Coating portions of the wet pre-treatment apparatus and the pipe that contact the corrosive effluent gas with a polymer, e.g. a fluorine resin such as TEFLON™ to prevent the corrosion is preferable.

[0027] The wet pre-treatment method of the effluent gas using wet pre-treatment apparatus 10 in accordance with the present invention shall be explained in detail below.

[0028] The effluent gas generated from the manufacturing processes of semiconductor or LCD devices is introduced into the wet pre-treatment apparatus of the present invention through effluent gas inlet 11 with the introduction direction thereof being tangential to the outer wall of upper cylindrical portion 17 of outer tubular member 10a. Atomized reagent 16 for pre-processing the effluent gas is introduced into wet pre-treatment apparatus 10 through reagent inlet 12 provided at the outer wall of upper cylindrical portion 17 of outer tubular member 10a with the introduction direction being tangential to the outer wall of upper cylindrical portion 17. As described above, the atomized reagent flows concurrently with the effluent gas.

[0029] The reagent used in wet pre-treatment apparatus 10 in accordance with the present invention includes neutral water, tap water, diluted solution of NaOH or $CaOH_2$, and electrolyzed water. The reagent is fed into atomizing spray nozzle 15 through reagent inlet pipe 14. When neutral water is used as the reagent, neutral water is introduced into nozzle 15 at a flow rate of about 100 to 500 cc/min, or more preferably 200 to 500cc/min. Since the preferred flow rate of neutral water is less than 500cc/min, wet pre-treatment apparatus 10 in accordance with the present invention can minimize the amount of waste-water while enhancing the treatment efficiency of the effluent gas. Therefore, the wet pre-treatment method in accordance with the present invention is environmentally friendly, reduces reagent usage, and lowers the manufacturing costs of semiconductor or LCD devices.